Trialling small-scale passive systems for treatment of acid mine drainage: A case study from Bellvue Mine, West Coast, New Zealand.

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And lastly, to the wonderful people that got me through this (you know who you are)…..

this is for you.

Abstract

Bellvue Mine is an abandoned coal mine near Rapahoe on the West Coast, South Island. This mine has been closed for over 40 years and is currently discharging acid mine drainage (AMD) into nearby Cannel Creek. Abandoned coal mines are very common on the Coast, and many of these "orphan" mines are also discharging AMD into the freshwater environment. AMD is a serious environmental issue because it is characterized by high dissolved metal concentrations and low pH conditions, both of which reduce the freshwater habitat and reduce the life-supporting capacity of rivers and streams. The existing geochemical knowledge of the site (and Cannel Creek) was limited to a single study undertaken in 2006 by Trumm and Cavanagh, which showed that Bellvue was responsible for over 60% of the AMD contamination to Cannel Creek.

This thesis presents the results of a 14-month research project that was undertaken at Bellvue Mine. The research was separated into two parts: the first aimed to improve knowledge and understanding of the background chemistry at the site and the chemistry of the receiving environment (Cannel Creek). To achieve this, a baseline geochemical survey was carried out from January 2013 to February 2014. The results of this survey were collated and seasonal trends in the AMD and Cannel Creek chemistry were analysed, and two principal conclusions were reached:

1) The pH of the AMD was very constant at ~2.5 over the course of the year, and
2) The dissolved metal concentrations (Fe, Al., Mn, Zn, Ni) showed clear seasonal patterns.

The second part of this research was an analysis of the performance of four different types of small-scale passive AMD treatment systems that were trialled over a 4-month period at the site.

- An oxidizing mussel shell reactor (MSO)
- A reducing mussel shell reactor (MSR)
- A sulphate-reducing bioreactor (Bioreactor)
- An anoxic limestone drain (ALD)

Of these systems, the MSO performed the best, decreasing the dissolved metal concentrations of Fe, Al, Zn, and Ni by over 90%, as well as increasing the pH to a constant level ~7-8 and increasing the alkalinity. Part two of the study has concluded that AMD can be treated successfully by a reducing mussel shell reactor and a bioreactor, but it is treated most effectively by an oxidizing

mussel shell reactor. It is recommended that a full-scale version of the MSO be installed at the Bellvue site.

1. Introduction

1.1. Background

Acid Mine Drainage (AMD) is a serious problem for environmental water quality scientists internationally, and New Zealand is no exception. In regions like the West Coast of the South Island where coal mining has a long history, AMD is a significant threat to water quality and the life-supporting capacity of the rivers and streams affected by it.

On such mine is Bellvue Mine north of Greymouth. This site has been abandoned since 1970 and has documented problems with AMD from the underground workings affecting nearby Cannel Creek. One of the biggest issues at the site is the lack of existing knowledge and scientific investigation of AMD at Bellvue. There has been one preliminary study by Trumm and Cavanagh (2006), which has given limited data on the environmental and chemical issues relating to remediation at the site.

The 2006 study found that Bellvue Mine discharge had a very low pH (~3) as well as elevated metal concentrations compared to the adjacent waterway. This chemistry makes the drainage uninhabitable for most aquatic organisms, as well as reducing the suitability of the receiving waters, Cannel Creek, by lowering the creek pH to 3.55 and increasing dissolved metal concentrations in the water. This has reduced the ecological value of Cannel Creek as well as the downstream environment.

The present research aimed to advance the science of passive AMD treatment at sites like Bellvue, by way of trialling small-scale passive treatment systems and measuring their performance over time. The selection and design of these systems was dependant on having a good understanding of the existing background geochemical conditions at the site; and using the existing literature from similar experiments conducted in New Zealand and overseas.

1.2. Coal Mining and the AMD problem

Coal is an essential resource for most primary industries worldwide, and is commonly used for activities like steel-making and electricity production. The annual end of financial year report produced by New Zealand's largest coal producer, the state-owned enterprise Solid Energy, gives evidence to the demand for and use of New Zealand coal. 3.9 million tonnes of coal were produced in 2013 and exports are divided into coal type: coking (57%), semi-soft (24%), and thermal (19%). The largest importer of New Zealand coal is India (49%) followed by Japan (26%), China (16%) and South Africa (9%), while national coal demand is primarily for steel (39%) and electricity (36%). The dairy industry is also an important consumer (11%), with other industries including meat, cement, timber processing, industrial processing, health, and wholesalers making up the remainder of coal consumers in New Zealand (Solid Energy, 2013).

The increase in demand for coal has seen production values grow considerably over the last decade, both in New Zealand (Figure 1.1) (MBIE, 2014 (B)) and overseas (EIA, 2014). This has been accompanied by an increase in the impacts the mining process has on the environment. The most common environmental impact associated with coal mining is acid mine drainage (AMD) (Black et al., 2005).

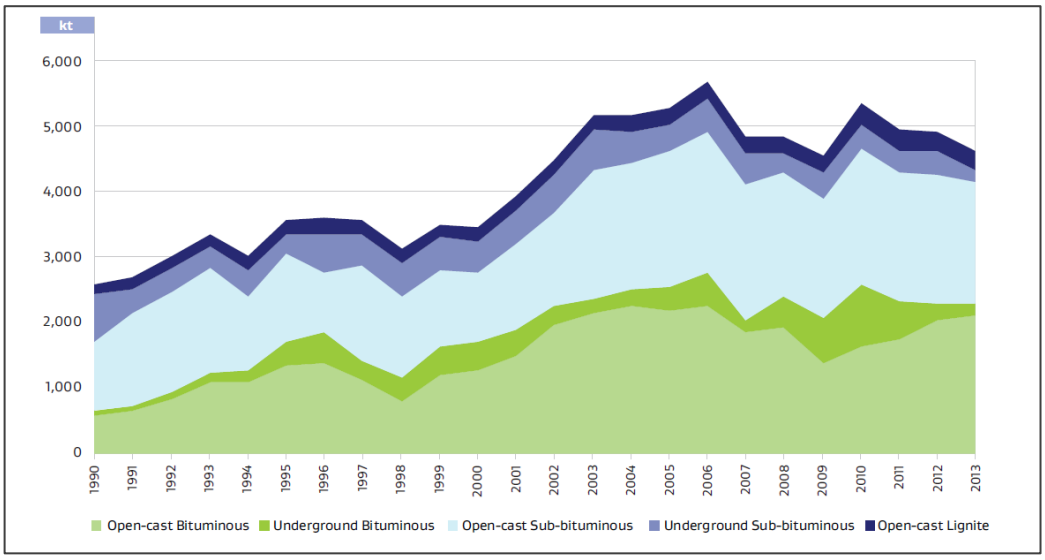

Figure 1.1 Coal production in kilo tonnes from 1990 to 2013 in New Zealand. Volumes have doubled since 2000, although the effect of the 2007-2008 global financial crisis caused a drop in production. (Modified from the MBIE's "Energy in New Zealand", 2014).

1.2.1. AMD Generation

AMD is the biggest environmental issue faced by the mining industry worldwide (Brown et al., 2002), and is caused when sulphide minerals in coal are exposed to water and oxygen (Alarcón León & Anstiss, 2002; Blowes et al., 2004; Brown et al., 2002; Davies et al., 2011, Pope et al., 2010) generating sulphuric acid and various metal compounds (Hogsden & Harding, 2012). The chemical composition of the metals in the AMD is determined by the sulphide minerals that were present in the coal, the most common of which is pyrite, FeS_2 (s) (Skousen et al., 2000). Blowes and Ptacek (2004) summarize the process of AMD generation, which starts with the oxidation of pyrite by atmospheric oxygen, releasing dissolved ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and acidity (H^+):

1.1) $$FeS_2(s) + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

The Fe^{2+} that is released by this step can be oxidized to Fe^{3+} if there is enough dissolved oxygen available, in a reaction that consumes acidity:

1.2) $$Fe^{2+} + \frac{1}{4}\,O_2 + H^+ \leftrightarrow Fe^{3+} + \frac{1}{2}\,H_2O$$

At pH greater than 3.5, Fe^{3+} is not soluble and precipitates as ferric hydroxide $Fe(OH)_3$(s), the end result of which is a decrease in pH:

1.3) $$Fe^{3+} + 3\,H_2O \leftrightarrow Fe(OH)_3(s) + 3\,H^+$$

At low pH (<3.5), Fe^{3+} is soluble and will dominate over oxygen as the oxidizing agent (Brown et al., 2002). This occurs in a reaction that is very acid-producing and much quicker than using oxygen, because electron transfer for Fe^{3+} is more efficient compared to O_2:

1.4) $$FeS_2(s) + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+$$

The overall balance of the AMD generation process is acid-producing. Aluminosilicate dissolution, of K-Feldspar for example, is acid-consuming but it is not rapid enough to have a significant buffering effect (Equation 1.5) (Blowes et al., 2004). It does free up Al^{3+} which then becomes available to form precipitates, although this process occurs slowly at low pH. Once pH rises (≥ 4.5), the rate of Al-precipitation will also increase (Nordstrom 2011).

1.5 $$KAlSi_3O_8 + 4\,H^+ + 4\,H_2O \leftrightarrow K^+ + Al^3 + 3\,H_4SiO_4^0$$

In acidic conditions (pH <4), metals tend to stay dissolved in solution (Nordstrom, 2011). When they do precipitate, it is usually as a pyrite oxidation product like goethite (α-FeOOH), oxyhydroxy-sulphates, or sulphate mineral. These secondary minerals are important because they affect the amount of acidity released during the pyrite oxidation process. Iron precipitates in particular, such as goethite, schwertmannite ($Fe_8(OH)_{5.5}(SO_4)_{1.25}$) or jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$), can have a significant effect on the environment (Sullivan & Bush, 2004).

Fe oxidation (Fe^{2+} to Fe^{3+}) occurs naturally as an abiotic (chemical) process, but is also facilitated by microbial activity. Iron-oxidizing bacteria are most active between pH 2 to 4, and so in AMD with high acidity (pH < 3) microbial activity has an important effect (Brown et al., 2002).

1.2.2. Environmental Impact of AMD

AMD generation is the result of a natural process that has been exaggerated by anthropogenic activity (mining). Discharges that are high in dissolved metals, especially Fe, and/or low in pH will have an important impact on receiving waters (Younger, 1997). Fe precipitates create thick layers of ferric hydroxides on streambeds which decrease the aesthetic appeal of the waterway, as well as smothering the substrate and benthic organisms. The hydrological interactions between the stream, hyporheic zone (the zone where surface water and groundwater mix beneath a streambed), and groundwater system are also altered because this layer decreases the permeability of the stream substrate, as well as preventing photosynthesis and consuming dissolved oxygen required by aquatic organisms living in these zones (Younger 1997). Dissolved metals in the water column pollute the water and reduce the alpha and beta diversity of the stream by creating a habitat that only pollution-tolerant species can survive. pH can also have a deleterious effect on stream biota, but not to the extent that dissolved metals do (Allan & Castillo, 2009), because excess metal concentrations have toxic effects on organisms. Heavy metals in streams are particularly damaging because they are not removed from aquatic ecosystems by natural processes, but instead are accumulated or transported to other systems (Harding, 2005).

The effects of AMD are site-specific, and are constrained primarily by the geology and hydrology of the area. The geology determines the physical and chemical qualities of contaminants that are

available in minerals in the deposit. The hydrology influences the rate and scale that these contaminants are mobilised at (Nordstrom, 2011).

1.3. AMD in New Zealand

The growth in the New Zealand coal industry over the last decade has been accompanied by an increase in the research and understanding of the effects that mining has on the environment and the actions taken to reduce or prevent these (Blowes et al., 2004; Brown et al., 2002; Younger et al., 2002). Government legislation around mining is set out in the Crown Minerals Act 1991 (MBIE, 2014 (A)) and the Mineral Programme for Minerals (Excluding Petroleum) 2013 (MBIE, 2013). Any environmental effects associated with mining activities are governed by the Resource Management Act (RMA) of 1991 (MfE, 2014). Under the RMA, local authorities (Regional Councils) are responsible for managing the effects of mining activities on the environment, including fresh waters (Simcock & Ross, 2014).

While mining companies today are responsible for the cost and process of remediating any effects their activities have on the environment, this has not been the case historically. In areas like the West Coast of New Zealand which have a long history of mining (>100 years), the legacy effects of unmonitored coal mining activities have had a large and important impact on the environment of that region (Black et al., 2004; Pope et al., 2010). The historical contamination from coal mines that is widespread throughout the West Coast is managed primarily by local government in the form of the West Coast Regional Council , the state-owned enterprise, Solid Energy (previously the government department State Coal Mines), and the Department of Conservation (DoC). One issue that these groups face is in identifying the causes of and taking remedial action to reduce contamination at unoccupied mine sites, which are informally referred to as ‘orphan’ mines.

Rehabilitation at these sites is not easy. Factors such a climate and topography mean that not all types of remediation option may be suitable for a particular site. In exceedingly pluvial regions such as the West Coast (with an average rainfall between 2500 and 4000 ml/year, NIWA 2014), rates of precipitation play an important role in determining how remediation will be undertaken, especially when dealing with contaminated water bodies. The cost of rehabilitating an orphan mine site is another limiting factor, as is the available information on mine site remediation which, although substantial, is “not necessarily applicable to the West Coast environment or tailored in a

way that is readily applicable to small mine sites with limited funds available for land rehabilitation." (Simcock & Ross, 2014)

1.4. Study Area

This research was conducted at the Bellvue Mine site on Cannel Creek, 2 km north of Rapahoe, near Greymouth, West Coast (Figure 1.2.). This area lies within the Greymouth Coalfield and is located on the boundary between the Solid Energy coal mining licence (CML) and Crown-owned DoC land (Jim Staton, pers. comm.).

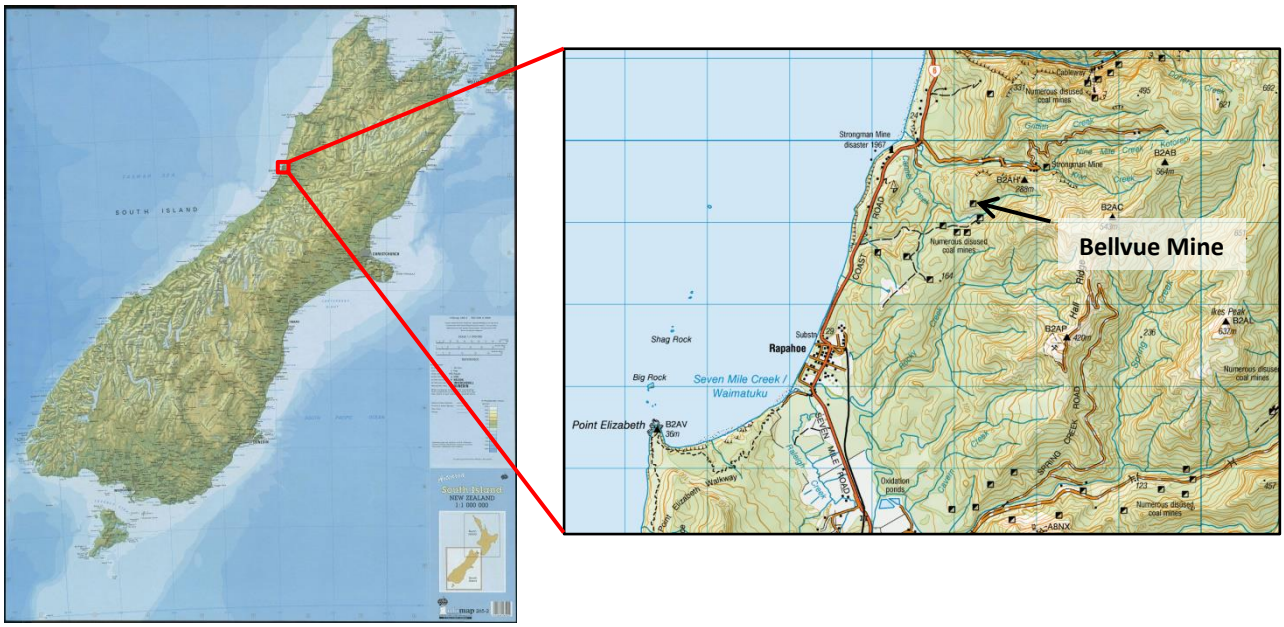

Figure 1.2. Map showing location of Bellvue Mine study area, West Coast, New Zealand. (Modified from Topo Map, LINZ, 2014).

Access to the site was via a 4WD track that had been recently cleared at the start of 2013, but degraded over the course of the study. An overview of the site itself is shown in Figure 1.3 (A). AMD collects in a pool in the mouth of the mine; this has been formed by the collapsed mine portal which is acting like a dam, restricting the flow of water from the flooded mine workings. The AMD flows out of the pool and down a 55m-high cascade (Figure 1.3 (B)). Based on the remaining coal truck rails, the piles of tailings nearby, the old timber lying on the slope, and the large concrete bins at the bottom, this was once a major route from the mine down to the old access road at the foot of the cascade. At the bottom is a large flat area around 80m^2, covered in coal tailings, small pebbles and gravels, and a hard oxidized layer caused by AMD precipitates

cementing the pebbles and gravels and creating a concrete-like substrate (Figure 1.3 (C)). There is little to no plant growth up to this point. From here, the mine discharge drops down again, another 3 m, to Cannel Creek. The discharge point into the Creek is steep and heavily eroded. Cannel Creek flows in a NW-SE direction, joining up to the main water, 9 Mile Creek, a kilometre or so downstream.

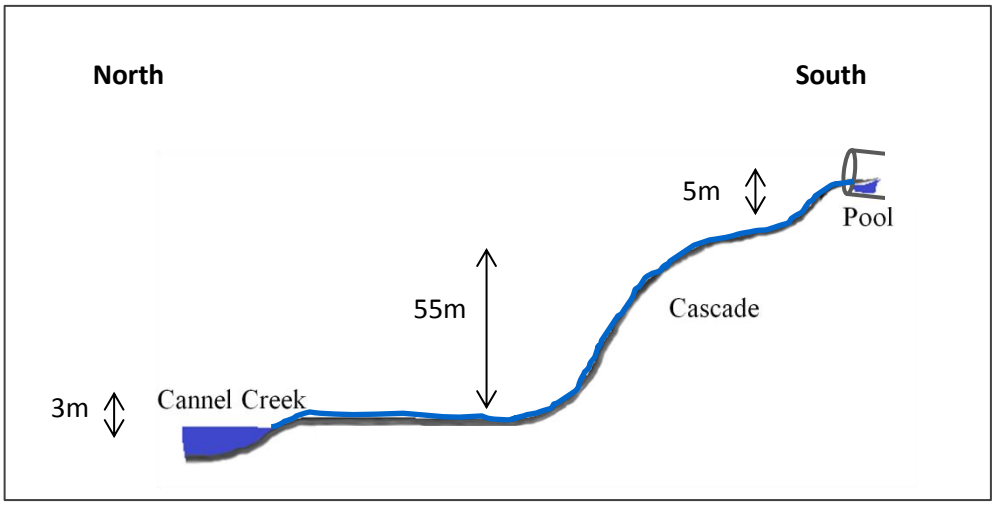

Figure 1.3 (A). Basic schematic of the Bellvue Mine site and direction of flow from the mine pool at the top of the slope down into Cannel Creek.

The flow of AMD at the site is controlled, to some extent, by the drainage morphology of the pool. The pool appears to discharge naturally through a small pipe-like feature which runs beneath the collapsed mine portal that blocks the mine entrance and forms the barrier that created the pool. This “pipe” cannot be seen underneath the rubble of the portal, apart from the little bit which emerges at the top cascade, and so any changes to its shape or size during the sampling period were unclear. This pipe appears to be a semi-permanent fixture, and it therefore acts like a drain for the pool. This makes it advantageous for this study because it creates a constant stream of AMD, the main discharge channel, which is small enough to be easily captured by a v-notch weir and measured.

The surrounding area is heavily forested with native trees and scrub. Gorse is very common, vegetating areas that had previously been cleared by mining or forestry (milling of the mine timbers). The climate is variable and seasonal, with the highest rainfall in spring (680 mm in 2013) and summer being the driest period (271 mm for 2013). The average annual temperature for the area is between 10 -12^{o}C (NIWA, 2014).

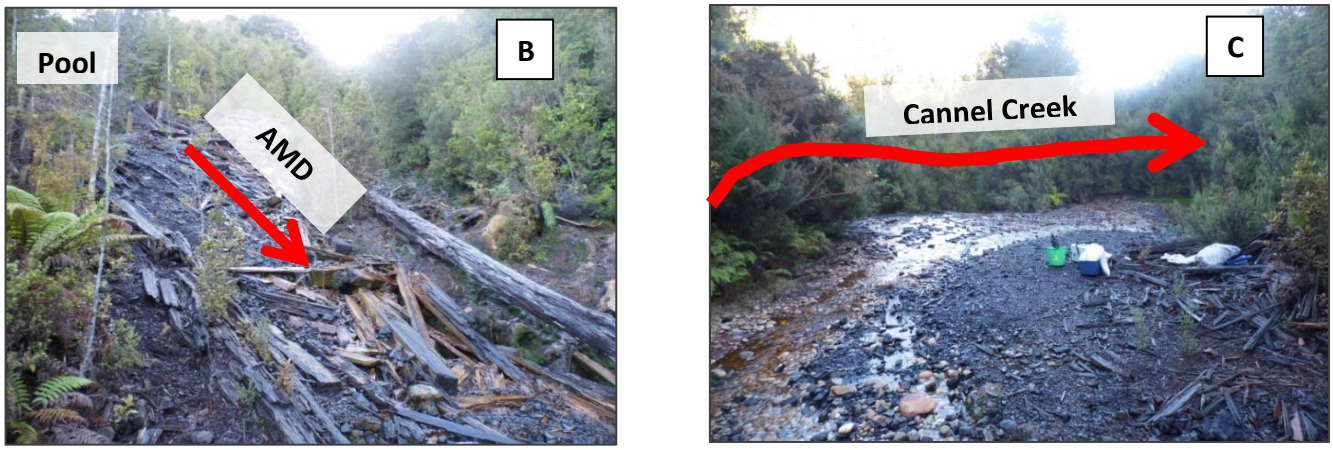

Figure 1.3 (B) View of the cascade site, with the location of the pool indicated at the top of the site and the direction of flow indicated by a red arrow. **(C)** View of the bottom half of the site, showing the open area of where treatment systems were installed. Canal creek flows from left to right and the location and flow direction is marked by a red arrow.

1.5. Mine History and Geology

The first recorded work at Bellvue Mine was in 1927 by the Bellvue Co-Operative Party. This was an extension to the seam being worked at nearby James Mine to the southeast of Cannel Creek. By 1932 the Mine had transferred ownership to Hadcroft and Party, and the working were exhausted by 1941 (Gage, 1952; Jim Staton, pers. comm.). At this point a new prospect was opened up on the north bank of Cannel Creek, presumably in the area that is now part of the study site. This area, M96, was worked using the pillar-extraction method from 1941 until 1965, after which no more reports can be found (Gage 1952, Jim Station, pers. comm.). The last available record is a mine plan from Bellvue Mines Limited, with the description “Ceased Production April 1970” written on it (Jim Staton, pers. comm.).

During the period from 1941 to 1965, coal was mined using the block-and-pillar extraction method, after which a surface endless rope gravitational haulage system transported the coal to the railway yard at Rapahoe (Gage, 1952). The coal at Bellvue itself was never directly analysed, but the nearby James Mine had a range of analyses performed, and the coal was described as a high-volatile coal; being "much duller and more homogenous than most coals and approach(ing) the composition of cannel coals", having a high sulphur and high hydrogen content. What is interesting is the mention that "Bands and lenses of pyrite occur in a few New Zealand coals, notably the James coal of the Greymouth Coalfield" (Gage, 1952; Suggate, 1959, pp. 14 and pp. 27).

1.5.1. Regional and Local Geology

Bellvue Mine is located in the Eocene Brunner Coal Measures (45-40 Ma), which unconformably overlie the Paparoa Coal Measures of Late Cretaceous to Palaeocene age (97-55 Ma) (Figure 1.4). The basement below the Paparoa Coal Measures is the Ordovician Greenland Group. There is a conformable and gradational change from the Brunner Coal Measures into the overlying marine sediments that make up the Kaiata Formation (Eocene) (Gage, 1952; Nathan et al., 2002).

1.5.1.1. Paparoa Coal Measures

These Late Cretaceous to Palaeocene rocks lie beneath the Brunner Coal Measures. They are made up of seven members of a non-marine sequence of fluvial conglomerates, sandstone, mudstone, and coal seams. The uppermost unit, the Dunollie Member, is increasingly quartzose at the top, and this has been attributed to chemical breakdown during the change from uplift and erosion in the late Palaeocene to regional extension in the early Eocene (Nathan et al., 2002).

1.5.1.2. Brunner Coal Measures

These are the oldest Eocene sedimentary rocks present in the stratigraphic record. They were formed during marine transgression and are made up of quartz sandstone, conglomerate, carbonaceous shales, and coal seams up to 10m thick (Nathan et al., 2002). Gage (1952) noted that the coal seams encountered at Bellvue and the nearby James Mine were inconsistent in both seam thickness and quality.

1.5.1.3. Kaiata Formation

This unit is widespread over the Greymouth and Buller region and consists of a massive, dark-brown mudstone. In the Rapahoe region that Bellvue lies in, this formation has been given the local variety name Island Sandstone, to differentiate it from the general mudstone that makes up most of the Kaiata Formation (Gage, 1952, Nathan et al., 2002).

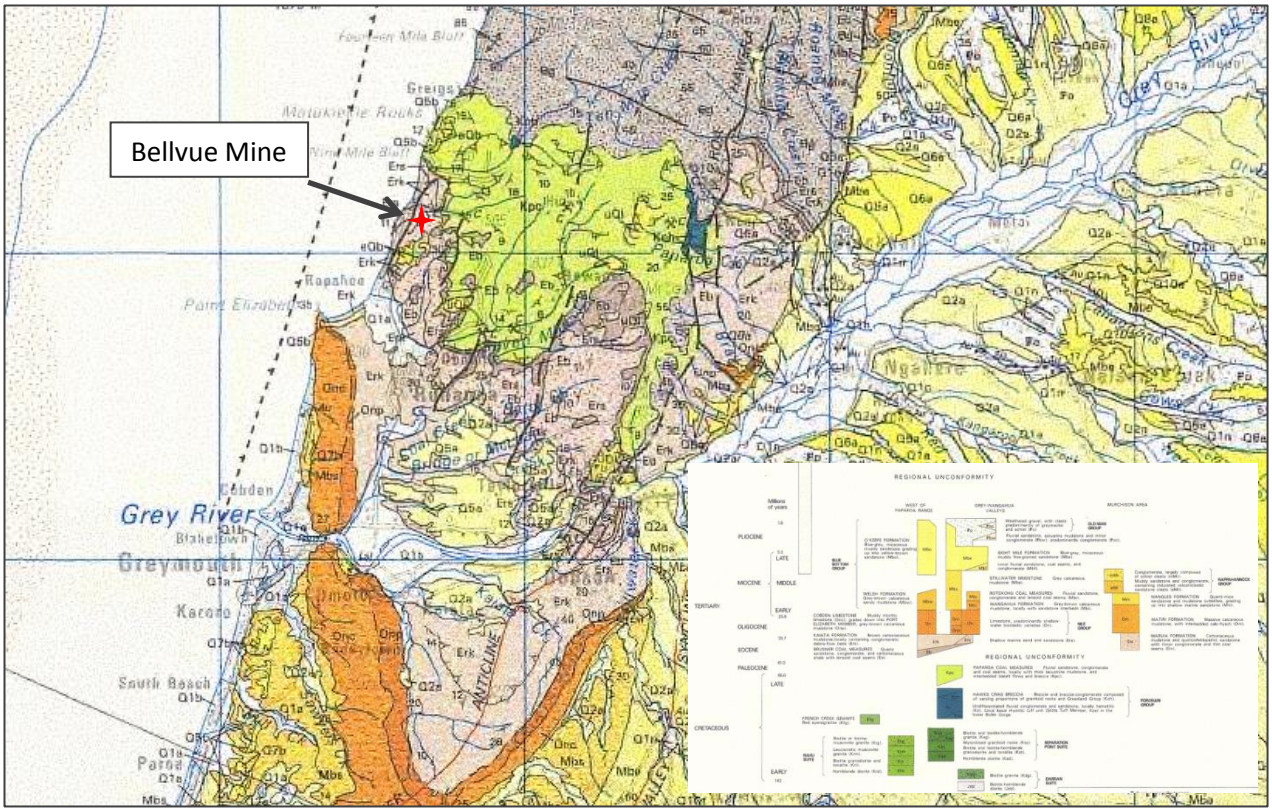

Figure 1.4. Geological map of the Rapahoe area, with the location of Bellvue Mine marked in red. Bellvue sits close to the boundary of the Brunner Coal Measures and Paparoa Coal Measures, but the mine itself is located in the Brunner Coal Measures. (Modified from Nathan et al., 2002)

1.6. Research Aims

This research trialled a range of small-scale passive treatment systems for AMD discharging from an abandoned coal mine on the West Coast of the South Island of New Zealand, Bellvue Mine. It is anticipated this will help environmental managers and scientists to make informed recommendations as to the best possible option for AMD remediation at the site.

The research aimed to increase knowledge of the existing chemistry of the mine discharge at the site, and offered an excellent opportunity to trial a range of passive treatment techniques, some of which are only recently-developed, in a timely, cost-effective manner. The results of this investigation can be used to help make a scientifically robust, informed decisions regarding management of the serious environmental problem that AMD poses at this site. It also allowed for collaboration with international AMD researchers and expanded understanding of passive treatment systems, some of which were employing relatively new technologies, at an international level.

1.6.1. Thesis Objectives

- Expand the existing database of background water chemistry and seasonal trends at the site
- Install trial passive treatment systems at the site, based on the data collected during the background monitoring
- Monitor changes to the chemistry of the treated AMD from each system
- Compare and contrast the results of different systems , some of which employ newly-developed technologies
- Use the results of the treatment regime to make recommendations for the best type of full-scale system to install at the site

1.7. Thesis Format

This thesis is organized into five chapters. The current chapter introduces the project background and details the current state of the acid mine drainage (AMD) issue, particularly in New Zealand. A description of the site and aims of the project; regional and local geology; and the history of Bellvue Mine are included to give context to the research.

Chapter Two presents the geochemical issues at the site, and the survey methodology that was used to investigate the water quality and water chemistry parameters that define Bellvue Mine AMD. The results of the geochemical survey are presented for each site, and summarized to show seasonal trends.

Chapter Three starts with a review of the existing literature on AMD treatment, and in particular, the types of passive treatment that have been used in the present research. It details the reasons why these systems were chosen, the design that was used for each, and how they were installed and monitored in the field. The results of the 4-month treatment study that was undertaken are presented at the end of the chapter.

Chapter Four outlines the issues that each treatment systems encountered, and analyses why these issues arose and possible changes that could be adopted in future work. It finishes with a summary of the results of the study and the implications that the findings of this research have for future passive AMD treatment in New Zealand.

Chapter Five presents an overview of the project; reiterating the objectives of the research, the main outcomes of the geochemical monitoring studies and field trials, and concluding with the analysis of the performance of the main treatment systems.

2. Geochemical Site Characterization

2.1. Introduction

Bellvue is an abandoned coal mine that has been derelict for the last 40 years. A 12-month sampling programme was undertaken at the site to monitor the baseline water chemistry for AMD in terms of seasonal and temporal changes from the pool down to Cannel Creek. This programme was run using a monthly chemical sampling regime, and various water quality parameters (temperature, dissolved oxygen (DO), electrical conductivity (EC), and pH), were measured at the time of sample collection.

Once collected, samples were then analysed by Hills Laboratories in Hamilton, New Zealand, following their pre-established chemical analysis methods (for a full list of tests see Appendix I) for dissolved concentrations of five key metals (iron (Fe), aluminium (Al), manganese (Mn), zinc (Zn), and nickel (Ni)), alkalinity, and sulphate. This first part of this chapter details the location of the sampling sites and the reasoning behind the site selection process; the sampling methodology that was used to collect the samples in-field; and the limitations of the sampling process and the implications it has for the results of this baseline water chemistry survey.

The second part presents the chemical results of the survey, and summarises the AMD issue at Bellvue Mine based on a 12-month sampling period.

2.2. Site Conditions and Sample Locations

Six sites were selected to conduct a baseline water chemistry survey at:

- The mine pool (the source of AMD)
- Two sites down the cascade, the top cascade and the mid cascade
- The bottom of the cascade
- Two sites in Cannel Creek, upstream and downstream of the Bellvue discharge point.

Each site was marked on a map to ensure consistent sampling, and a schematic of the site (not to scale) was created to show where each AMD sampling site was (Figure 2.1).

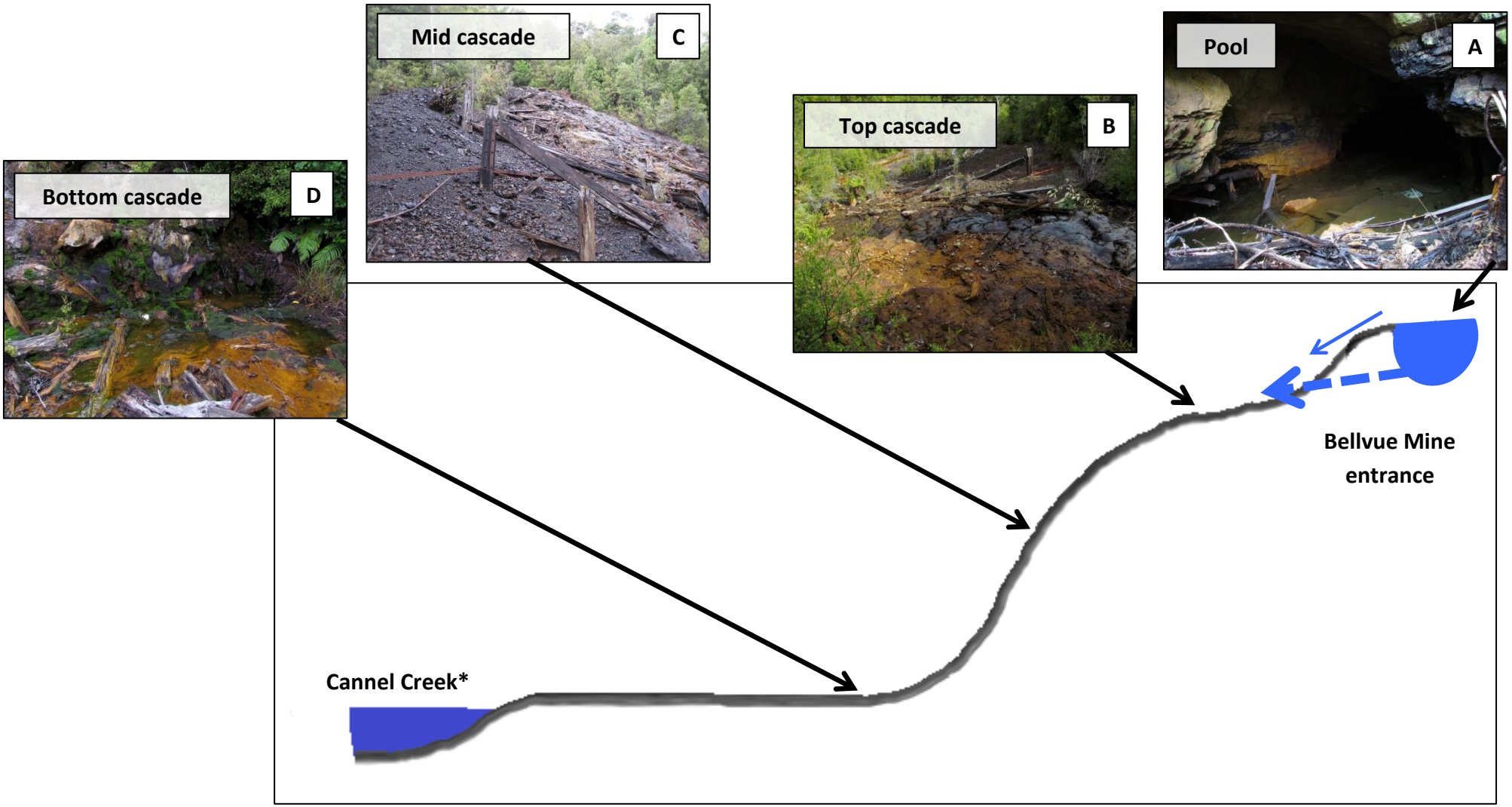

Figure 2.1. AMD sampling sites along the Bellvue Mine discharge, indicated by black arrows, with a reference picture attached: **A)** pool site (A), **B)** top cascade site (B), **C)** mid cascade site (C), **D)** bottom cascade site (D). Flow direction from the pool is marked by the blue arrows. The main discharge is from the base of the pool (represented by a dashed line because this pathway was not seen and is inferred). A smaller flow intermittently discharges over the top. (*)Cannel Creek had two sampling sites, which are discussed below. Photos courtesy of D. Nobes and D. Trumm (2013).

The Bellvue Mine discharge flows into Cannel Creek and two sites, one upstream of the AMD inflow and one downstream, were sampled (Figure 2.2).

Figure 2.2. A) Upstream Cannel Creek sampling site (E). Samples were collected from the small pool in the centre of the image. **B)** Downstream Cannel Creek (F). Here the flow was faster and samples were collected to the mid left of the image. Photos courtesy of D. Nobes and D. Trumm (2013).

Each location, both for the AMD and Cannel Creek sites, was chosen based on ease of access, reliability of flow and coverage of the entire site. Some parts of the AMD discharge, especially down the cascade, were very low volume and only flowed intermittently. The AMD sites were chosen to cover the entire discharge area, from A to D. The B and C sites were added based on the findings of the 2006 report by Trumm & Cavanagh, which showed that the chemistry of the discharge changed significantly between A and D, and by adding these two sites in it was possible to gain a better understanding of where these chemical changes were occurring and why. The E and F sites were chosen as close as possible to the point where the AMD was entering the stream, but access was made difficult by steep banks and dense undergrowth at this point, so the site locations were adjusted to allow for this and moved back around 10 m each way.

2.3. Water Sampling

2.3.1. Sampling Protocols

A range of water quality parameters at all sites were monitored by field methods; these were pH, electrical conductivity (EC), temperature, and dissolved oxygen (DO). At the same

time, samples were collected for chemical analysis of pH, alkalinity, and dissolved metal and sulphate concentration.

A 2006 study of the site had shown five metals in particular were elevated in the AMD – Fe, Al, Mn, Zn, and Ni, in order of most concentrated to least (Trumm & Cavanagh, 2006). To better direct the project and simplify the amount of analysis that was required these key metals were the only ones monitored on a monthly basis. A full suite analysis of the A and D sites was conducted on a quarterly basis. All chemical analyses were performed by Hills, following the relevant APHA Standard Methods (for a full description see Appendix I)

Sites were sampled in an upstream direction; starting at F, followed by E, then the four AMD sites (D, C, B, and then A). Water quality parameters were measured using a calibrated PSI 556 MPS probe, which took measurements while chemical samples were being collected to ensure enough time for the probe to settle and improve the accuracy of the readings. Water chemistry samples with no head space were collected in Polyethylene sampling bottles provided by Hills. For the Cannel Creek sites, the sampling containers and analyses performed on each were as follows:

- Sulphate, pH, and alkalinity - 1x 250 mL sampling bottle, sample was unfiltered and unpreserved
- Dissolved metals – 1x 100 mL sampling bottle, sample was filtered using a 20 ml syringe and 0.45 µm membrane filters, and preserved in nitric acid (to ensure the metals stayed in solution and did not precipitate out).

For the AMD sites:

- Sulphate and pH – 1x 100 mL sampling bottle, sample was unfiltered and unpreserved
- Dissolved metals – same as for the Cannel Creek sites.

A full suite of metal and ion analysis of the A and D sites was conducted on a quarterly basis during 2013 (four samples: March, June, September and December) (Appendix I). The preserved dissolved metal sampling process for this was unchanged. A greater volume (1L) of unpreserved sample was collected to allow for the sulphate and pH analyses, as well as the additional total dissolved metals and ions analyses.

2.3.2. Fe Speciation

Trumm & Cavanagh (2006) measured dissolved iron concentrations at the site and found that it occurred in two forms, Fe^{2+} (reduced ferrous, soluble divalent) and Fe^{3+} (oxidized ferric, insoluble trivalent). The ratio of Fe^{2+}/Fe^{3+} changed between the pool and bottom cascade and in order to investigate where this occurred, Fe speciation testing was included in the sampling regime at all AMD sites. This was done using a portable photospectrometer, an Hach DR2800 model, which gave total Fe and Fe^{2+} measurements. Fe^{3+} was calculated as the remainder of the total Fe once Fe^{2+} was excluded.

Sampling for the total Fe and Fe^{2+} concentrations was conducted following the protocols set out in methods 8008 (total Fe) and 8146 (Fe^{2+}) of the Hach EPA-compliant Method Handbook (see Appendix I for details):

- The appropriate test (either total Fe or Fe^{2+}) was chosen from the stored programmes in the DR 2800.
- Blank preparation: to give more accurate results, the machine was zeroed before each test. This was done by filling a square sample cell with 10 mL of untouched AMD and running the DR 2800 on the 'Zero' function. This set a baseline that variation in Fe concentration could be measured from.
- Sample preparation and analysis: a clean, 25 mL graduated cylinder was filled with fresh AMD, and one FerroVer Iron Reagent Powder Pillow was added and mixed. The three-minute reaction period timer on the DR 2800 was then started (Figure 2.3). At the end of this period, a square sample cell was filled with 10 mL from the cylinder. This was then inserted into the cell holder in the DR 2800 in the correct orientation, after the outsides of the cell had been wiped dry. The 'Read' function then produced a concentration reading in mg/L.
- Total Fe was analysed first, then Fe^{2+}, and the results of each test were recorded when displayed.

Figure 2.3. View of the spectrophotometer and graduated cylinder (with AMD sample inside). The orange colour of the AMD shows that the reagent powder has been added and there is Fe in the sample. Photo courtesy of D. Nobes.

One issue with this method was the extremely high levels of dissolved Fe in the AMD, one of the main water quality problems at Bellvue. This caused a 'limit exceeded' error message to appear on the DR 2800 and erroneous readings were generated. To remedy this, a final test was done in March 2014 during which the AMD was diluted to a ratio of 1:100 AMD:distilled water for total Fe, and 1:5 AMD:distilled water for Fe^{2+}. This created baseline Fe concentrations low enough for the machine to measure.

2.3.3. Flow Measurement

Flow rate was used to calculate fluxes of metals and acidity from the pool and is needed to calculate the size of a full-scale AMD treatment system at the site. This was first measured using a bucket and timer method, followed by the installation of a v-notch weir in July 2013 which captured the entire flow at that point. Flow measurements were taken on average every two months. Flow was calculated from the time taken to collect a known volume of water. Each test was repeated at least three times and flow rate was averaged from this.

An Intech WT-HR 1m data logger was installed in the pool in July 2013 (Figure 2.4). This was set to take automatic readings of water height and temperature every 30 minutes. Roughly every 3 months the data was downloaded and analysed using the OmniLog Data Management Programme.

Figure 2.4. View of the pool showing the data logger after installation. The floor of the pool was very uneven so the fixed datum point for the logger is not an absolute zero for water height.

2.3.4. Limitations to the Sampling Regime

Monitoring was carried out on a monthly basis, and sites were all sampled on a single day, to ensure an accurate snapshot of the chemistry was achieved. The monthly sampling period however, only allows seasonal trends in chemistry to be calculated. This decision was necessary because of funding limitations and timing constraints, the field site being a 3.5 hour drive away; it was not feasible to conduct sampling on a more frequent basis.

The high level of iron precipitates in both Cannel Creek and the mine discharge made sampling difficult because any disturbance to the substrate dislodged fine particles of the precipitates and disrupted the sampling process. To avoid this, sampling was conducted in an upstream manner, so that any disturbance would not affect the site being sampled, and extreme caution was taken when sampling to avoid this.

The site itself created issues when sampling, given the difficult nature of the topography. Sites A, B, and C were all situated on or above a steep slope made of loose unstable coal tailings and rubble. This affected the site selection process and also caused delays when sampling between sites, because of the time it took to move equipment and set up at each new site.

2.4. Data Analysis and Key Results

2.4.1. Units of Measurement

Dissolved/ total metals and sulphate concentrations from water chemistry analyses by Hills were reported in g/m^2, as were the ionic compounds and other parameters measured in the quarterly full suite sampling (a full list Is provided in Appendix I). Total acidity, alkalinity, and hardness were reported as g/m^3 as $CaCO_3$, while bicarbonate was reported as g/m^3 at 25°C. Anion and cation analyses were reported in meq/L.

Water quality parameters were reported in pH units, °C (temperature), µS/cm (EC), and both mg/L and % for DO.

2.4.2. Flow Data

Flow was measured at site B and varied between 0.25 and 0.5 L/s, which is a surprisingly consistent flow rate. The average discharge from the pool over the 12 months that sampling was conducted is 0.35 ± 0.1 L/s. As well as the discharge, the level and temperature of site A was monitored every 30 minutes using a water logger over an 8 month period from July 2013 to February 2014. Water height ranged from 133 mm to 1075 mm above the base of the pool. There was a seasonal trend in water height, with the highest average level in October (mid spring, when precipitation was also at a maximum (NIWA, 2014)). There was not enough data to make long term trend observations, but average water height was relatively stable around 400-500 mm. Average water temperature increased as the seasons changed from mid-winter (July, the coldest month on average) to the end of summer (February, the warmest month on average). A summary of this is presented in Table 2.1 and the full range of data is given in Appendix I.

Table 2.1. Summary table showing average water height and temperature in the pool from July 2013 to early Feb 2014. February averages were from the first week only.

	Water height (above the pool base) (mm)			Water temp (°C)		
Month	**Min**	**Max**	**Avg**	**Min**	**Max**	**Avg**
July	133	657	413	1.7	11.1	8.3
August	440	753	505	3.30	11.6	9.27
September	404	823	494	3.55	12.1	9.21
October	452	1075	645	4.80	12.8	10.5
November	351	746	440	8.30	13.2	11.5
December	389	732	440	8.28	13.8	11.8
January	414	894	486	7.78	14.2	12.0
February	427	490	456	12.0	12.4	12.8

2.5. Water Chemistry Results

2.5.1. Average Data

A summary of the AMD chemistry at Bellvue Mine and Cannel Creek is presented in Table 2.2. The monthly sampling period means that seasonal trends in metal concentration and water quality parameters only are shown. Lowest average pH was measured at site A (pH 2.5), while sites B, C, and D were only slightly higher than this (pH 2.53, 2.57, and 2.51 respectively). After addition of Bellvue AMD, Cannel Creek dropped from an average pH of 5.47 (Site E) to 3.16 (Site F), and the EC increased from 54 to340 µS/cm on average.

Table 2.2. Summary of background chemistry from Bellvue Mine and Cannel Creek. Data was collected on a monthly basis from Jan 2013 to February 2014. The data are averaged over 14 months.

		Site name					
Chemical parameters		Pool (A)	Top cascade (B)	Mid cascade (C)	Bottom cascade (D)	U/s Cannel Creek (E)	D/s Cannel Creek (F)
pH		2.5	2.53	2.57	2.51	5.47	3.16
EC	µS/cm	1772	1671	1636	1754	54.06	340.0
DO	%	16.2	49.6	102	93.3	92.5	92.9
	mg/L	1.68	5.16	10.5	9.97	10.3	15.1
Dissolved metals							
	g/m³						
	Ca	54.3	50.4	50.6	52.9	2.53	10.5
	Fe	80.3	91.4	90.4	81.4	0.242	6.98
	Al	38.2	42.1	43.5	43.3	0.135	6.68
	Mn	0.733	0.811	0.831	0.837	0.008	0.169
	Zn	0.308	0.343	0.348	0.347	0.002	0.052
	Ni	0.116	0.128	0.130	0.131	0.001	0.028
Sulphate	g/m³	753	792	812	824	4.66	126

2.5.2 Pool Chemistry (Site A)

Site A pH ranged from 2.34 to 2.95, and total acidity (to pH 8.3) averaged 640 mg $CaCO_3$/L (420 - 990 mg $CaCO_3$/L). DO was lowest at A compared to the rest of the discharge and averaged 16.2 % (8 - 31.6 %), while EC was 1772 (1592 - 2049 µs/cm). Metals at highest concentration in the discharge were Fe, Al, Mn, Zn, and Ni respectively (Figure 2.5). At the pool site, Fe averaged 80mg/L (28 - 210 mg/L), Al averaged 38 mg/L (21 - 67 mg/L), Mn averaged 0.73 mg/L (0.46 - 1.22 mg/L), Zn averaged 0.308 mg/L (0.189 - 0.52 mg/L), Ni averaged 0.116 mg/L (0.073 - 0.187 mg/L), while sulphate averaged 753 mg/L (520 - 1280 mg/L).

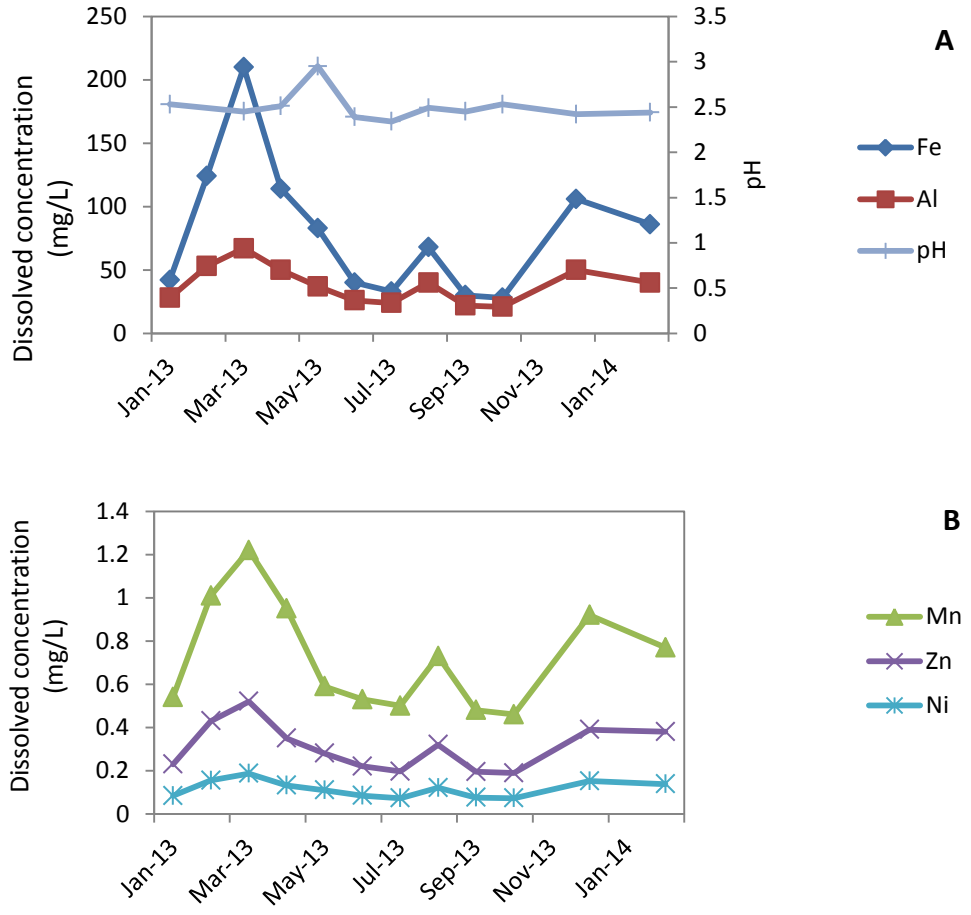

Figure 2.5. Average pH and metal concentration at site A at Bellvue Mine from Jan 2013 to Feb 2014. (A) pH, dissolved Fe and Al. (B) Dissolved Mn, Zn, and Ni.

In the averaged quarterly full suite analysis of AMD from the pool, nitrate ranged from 0.028 - 0.04 mg/L with an average of 0.034 mg/L, nitrite from 0.011 - 0.8 mg/L with an average of 0.406 mg/L, and total ammoniacal-N from 0.23 to 0.25 mg/L with an average of 0.24 mg/L. These metals all showed a range of values, but the variation was seasonal. Summer months

(December to February) had the highest metal concentrations, while winter (June to August) had the lowest. This is interpreted as a seasonal dilution effect from local precipitation and the same pattern (dilution in winter, concentration in summer) is seen from the A to D sites.

2.5.3. Top Cascade (Site B)

The next site downstream from A was site B, the top cascade. This sampling site had an average Fe concentration of 91 mg/L (34 - 210 mg/L), while Al averaged 42 mg/L (25 - 73), Mn averaged 0.811 mg/L (0.53 - 1.29 mg/L), Zn averaged 0.343 mg/L (0.22 - 0.57), and Ni averaged 0.128 mg/L (0.081 - 0.196 mg/L). Average pH was 2.53 (2.43 - 2.91), with an average sulphate concentration of 792 mg/L (530 - 1140 mg/L) (Figure 2.6). An abnormally high pH in May 2013 was not associated with any spikes or drops in metal concentrations at the same time. The range of metal concentrations is the same scale as site A, and the only noticeable change is to pH. The pH at site B was more variable, from 2.4 to 2.9.

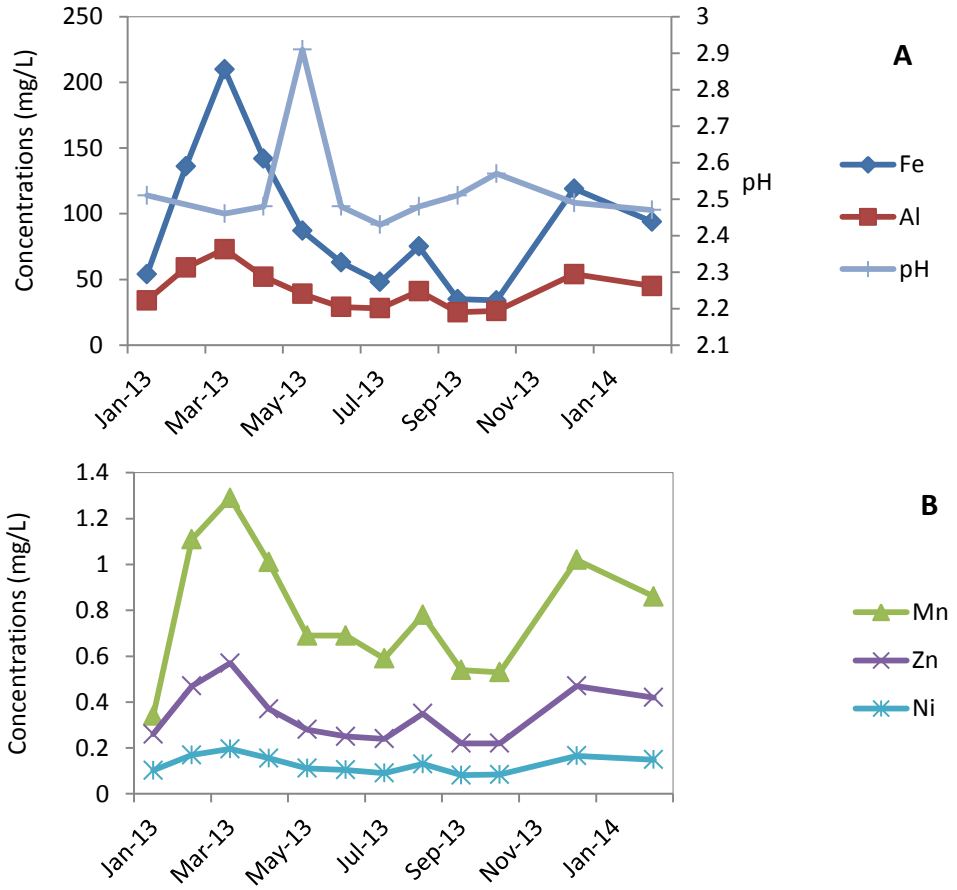

Figure 2.6. Dissolved metal concentrations and pH at site B. (A).Dissolved Fe and Al, and pH. (B) Dissolved Mn, Zn, and Ni.

2.5.4. Mid Cascade (Site C)

The pH at this site ranged from 2.43 to 2.9, sulphate averaged 812 mg/L (530 - 1250 mg/L) and metal concentrations averaged 90.4 mg/L (33 - 190 mg/L) for Fe, 43.5 mg/L (24 - 74 mg/L) for Al, 0.831 mg/L (0.53 - 1.28 mg/L) for Mn, 0.348 mg/L (0.21 - 0.56 mg/L) for Zn, and 0.13 mg/L (0.08 - 0.20 mg/L) for Ni (Fig. 3). Metal concentrations were more variable, and the peaks in Fe and Al, in particular, appear to lag behind those for sites A and B. This is complicated by the monthly sampling, which means that it hard to make inferences and patterns from the data.

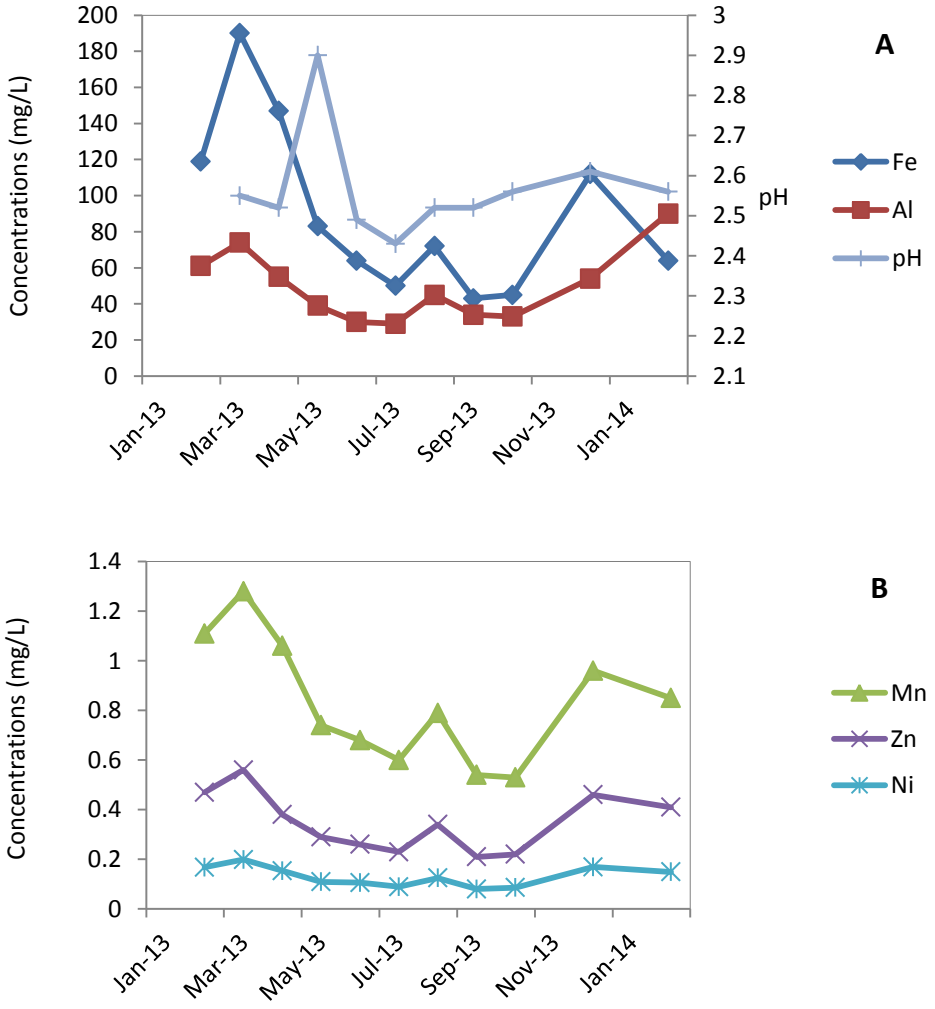

Figure 2.7. pH and dissolved metal concentrations at site C. (A)Dissolved Fe, Al, and pH. (B) Dissolved Mn, Zn, Ni.

2.5.5 Bottom Cascade (Site D)

This was the final sampling point on the Bellvue discharge, and at this site the pH ranged from 2.4 to 2.78, and sulphate averaged 824 mg/L (550 - 1360 mg/L). The average dissolved metal concentrations in the discharge are 81 mg/L (35 - 148 mg/L) of Fe, 43 mg/L (25 - 72 mg/L) of Al, 0.837 mg/L (0.53 - 1.30 mg/L) of Mn, 0.347 mg/L (0.22 - 0.53 mg/L) of Zn, and 0.131 (0.084 - 0.193 mg/L) of Ni. The seasonal trends in metal concentration at this site were still noticeable, but were less obvious because there was more variability in the data as a whole at site D. Manganese spiked in the middle of winter at this site, which is not able to be explained currently.

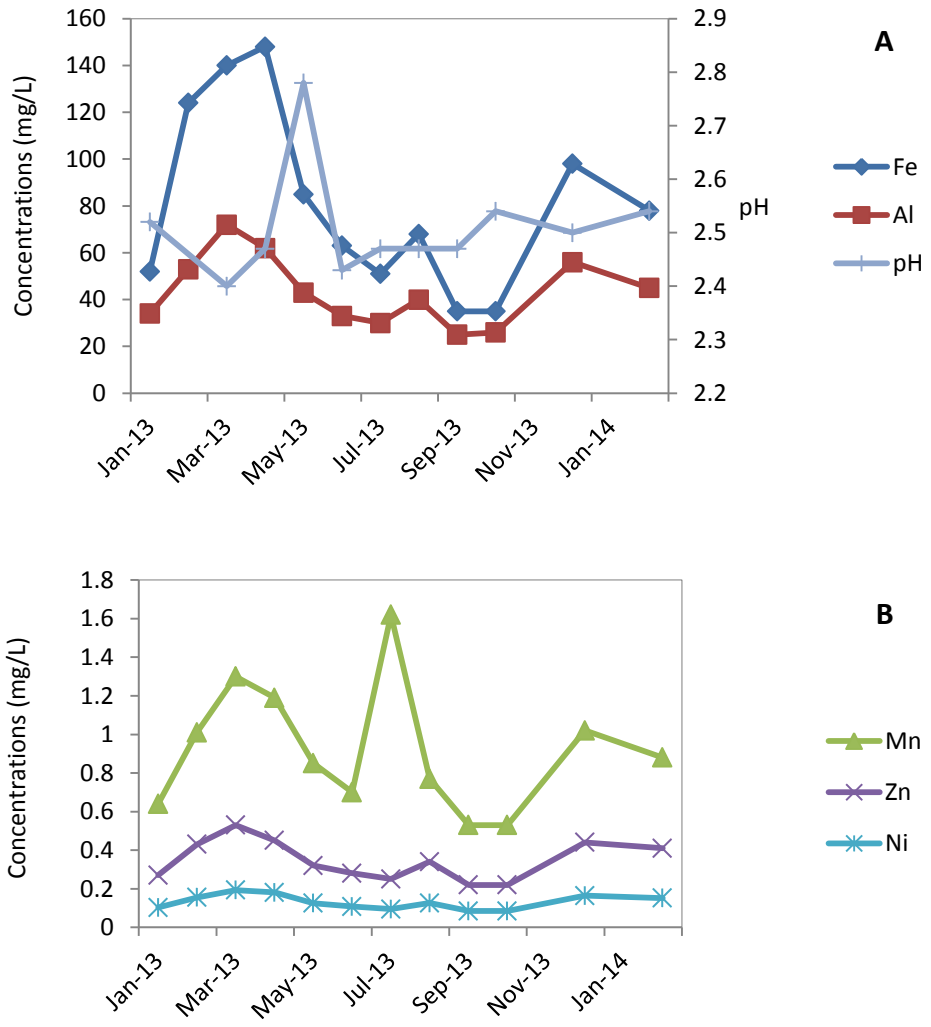

Figure 2.8. Dissolved metal concentrations and pH at site D. (A) pH and dissolved Fe and Al. (B). Dissolved MN, Zn, and Ni

2.5.6. Iron Speciation along the Cascade

Iron occurred in two forms at the site, and the dissolved concentration ratio of these two forms changed as the AMD moved down the cascade (Table 2.3). Fe^{2+} had the highest recorded concentrations at the pool (14.6%) and top cascade (21.9%) sites. At the bottom cascade, nearly all Fe^{2+} bad been replaced by Fe^{3+}, with just 1.46% remaining.

Table 2.3. Iron speciation change down Bellvue Mine Cascade. Data collected over a 60 minute period on 15 March 2014.

Site	Fe concentration (mg/L)			% Concentration	
	Total	Fe^{2+}	Fe^{3+} (Total - Fe^{2+})	Fe^{2+}	Fe^{3+}
Pool	71.0	10.4	60.6	14.6	85.4
Top Cascade	75.0	16.4	58.6	21.9	78.1
Mid Cascade	79.0	8.95	70.1	11.3	88.7
Bottom Cascade	103	1.50	101.5	1.5	98.5

2.6. Cannel Creek Sampling

2.6.1. Upstream Cannel Creek (Site E)

At this site the water quality was better than any other site sampled. It had a pH range from 4.60 to 6.26 and an average sulphate level of 4.5 mg/L (2.1 – 8.0 mg/L). The concentration of dissolved metals in the creek was also much lower than that of Bellvue Mine, with an average Fe of 0.242 mg/L (0.15 - 0.47 mg/L), Al of 0.135 mg/L (0.046 - 0.350 mg/L), Mn of 0.0083 mg/L (0.0049 - 0.0230 mg/L), Zn of 0.0022 mg/L (0.0012 - 0.0045 mg/L) and Ni of 0.0006 mg/L (0.0005 - 0.0010 mg/L), as shown in Figure 5.

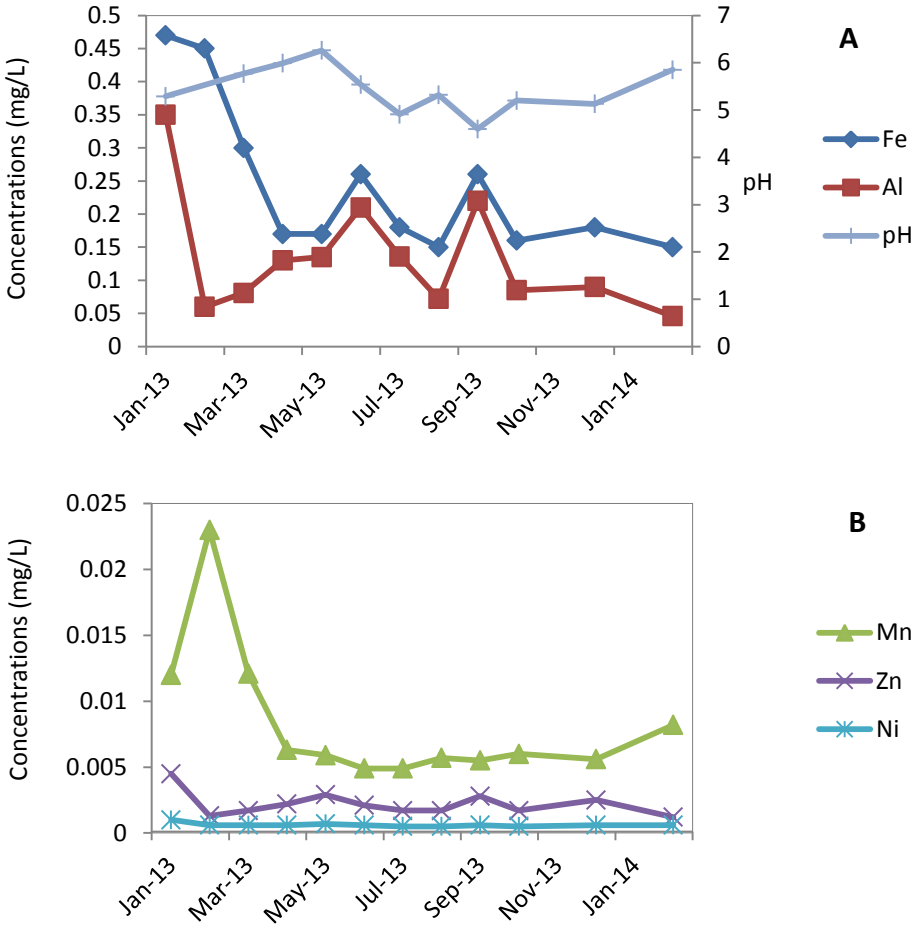

Figure 2.9. Dissolved metal concentrations and pH at site E upstream of the Bellvue Mine AMD discharge. (A) Dissolved Fe and Al, and pH. (B) Dissolved Mn, Zn, and Ni.

This site was relatively steady in regards to the pH (which stayed nearly constant between pH 5 and 6) and the less concentrated metals (Mn, Zn, and Ni). Fe and Al were more varied over the sampling period, but this was mainly due to a large spike in metal concentrations at the end of the summer period. Apart from this spike, metal concentrations did not fluctuate more than 0.2 mg/L. Cannel Creek has one mine, Jubilee Mine, discharging AMD into it by the time the stream reaches this point, and this AMD may be the source of the metals and the reason for their changes over time.

2.6.2. Downstream Cannel Creek (Site F)

At this site, Bellvue Mine AMD had entered and mixed with Cannel Creek. pH decreased to a minimum of 2.76 (with a maximum of 3.62), while sulphate increased to an average of 126 mg/L (15.1 - 430 mg/L) - a good indication that AMD, as opposed to another environmental source is contributing to the increase in dissolved metals and other geochemical contaminants in the creek. The average dissolved metals (shown in Fig. 6) are 6.98 mg/L (0.89 - 33 mg/L) of Fe, 6.68 mg/L (0.55 - 26 mg/L) of Al, 0.169 mg/L (0.0197 - 0.520 mg/L) of Mn, 0.052 mg/L (0.0074 - 0.210 mg/L) of Zn, and 0.028mg/L (0.0024 - 0.131 mg/L) of Ni.

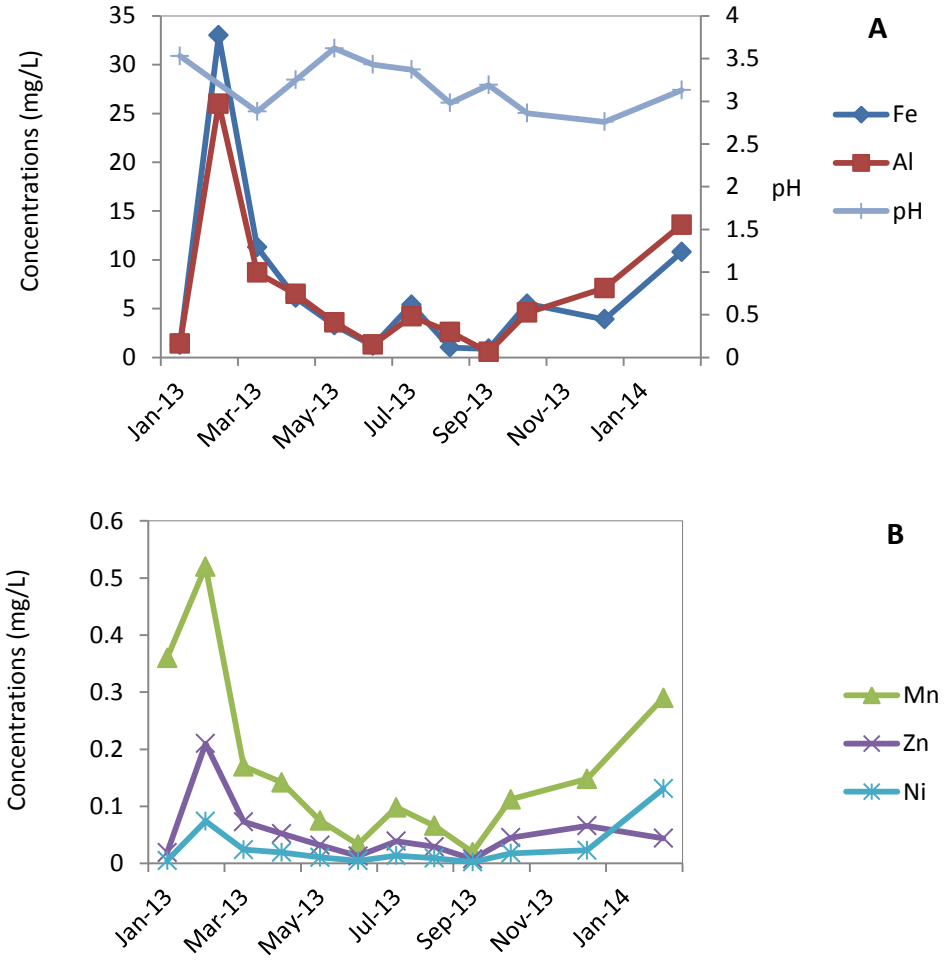

Figure 2.10. Dissolved metal concentrations and pH at site F. (A) Dissolved Fe and Al, and pH. (B) Dissolved Mn, Zn, and Ni.

This site showed very clear seasonal trends. There was a very large (six-fold increase for Fe and slightly less for the other metals) spike at the end of the summer months, when local precipitation was at its lowest. Conversely, the lowest metal concentrations and highest pH

levels are seen in winter, when the dilution effect from precipitation is most obvious. Another trend that emerged was the difference between site E and site F. The increase in dissolved metal concentrations and sulphate indicate that the water chemistry in Cannel Creek was degraded by the influx of Bellvue Mine AMD.

2.7. Summary

Bellvue Mine AMD is characterized by high dissolved Fe and Al particularly, as well as elevated Mn, Zn, and Ni. pH is typically low (< 2.6 at most sites) and DO and conductivity change between the pool site at the top of the mine site and the bottom.

The background AMD chemistry at the site showed seasonal variations. pH was very steady at the pool site, maintaining a level just under 2.5, apart from a small fluctuation early in the sampling period. Downstream sites (top cascade, mid cascade, and bottom cascade) showed increasingly variable pH as other parameters like DO and metal concentrations changed in the discharge. The pool site chemistry overall was more stable than the downstream sites, and this influenced the overall chemical patterns at the site. Perturbations to dissolved metal concentrations occurred around the same time at each site, and local precipitation played a part in the chemistry of the AMD. Higher metal concentrations were recorded over the summer months, when there was less dilution; while the lowest concentrations were recorded in winter/spring, when precipitation was highest.

3. Passive Treatment Trials

3.1 Overview

AMD is caused by physical and chemical weathering of sulphides like pyrite (Behum et al., 2011; Kaksonen & Puhakka, 2007; Larson et al., 2014; Trumm et al., 2008, Ziemkiewicz et al., 1997). The process of coal mining exposes pyrite and increases the available surface area for oxidation, thereby increasing the occurrence of AMD. Discharges that are high in dissolved metals, especially Fe, negatively impact the waterways they flow into (Younger, 1997) because they pollute the water and create a habitat that only pollution-tolerant species can survive. pH can also affect stream habitats, but not to the extent that dissolved metals do (Allan & Castillo, 2009), because excess metal concentrations have toxic effects on organisms.

Prevention of AMD is one option for controlling this pollution (Kaksonen & Puhakka, 2007), and this is done by excluding oxygen so that pyrite oxidation cannot occur. If this cannot be achieved, however, or if the mine in question has been abandoned and AMD is already occurring, then treatment options to reduce the impact of AMD – by reducing the level of metals and acidity in the discharge - is needed (Larson et al., 2014; Trumm et al., 2006). There are two main types of AMD treatment, active and passive (Mackenzie et al., 2011; Trumm, 2010; Trumm & Watts, 2010).

Active treatment is best suited to small areas, mines that are still operating, sites with high flow conditions, and/or sites that have power and personnel to monitor the active treatment systems (Trumm, 2010). The water is treated by adding alkali materials which neutralize the acid and promote metal precipitation (Hengen et al., 2014; Ziemkiewicz et al., 1996). This is costly, and must be continued even after the mine has shut, because AMD will continue to be produced for many years (Ayora et al., 2013; Crombie et al., 2011). Where this is not practical, such as orphan mine sites like Bellvue, passive treatment is the best option because these sites often have more stable chemistry and flow rate (Trumm, 2010).

Passive treatment systems require little or no maintenance (Ziemkiewicz et al., 1997), have a much longer life expectancy (because they are engineered to last for >25 years), and suit

sites that are not operational and/or have low flow conditions (Ayora et al., 2014; Davies et al., 2011). They can be better alternatives because they are less expensive and rely on natural geochemical and biological processes to neutralize the acid and reduce metal concentrations in the discharge (Trumm et al., 2008), and do not require addition of chemical reactants as often as active systems do (Hengen et al., 2014).

Active treatment:

- **short term**
- **requires constant addition of reactive material**
- **costly in the long term**

Passive treatment:

- **long term (>10 years)**
- **does not require as much maintenance**
- **material costs are high to start with, but overall uses less materials**

3.2 Passive Treatment Systems

3.2.1. Principal Types

Choosing the right type of passive treatment systems for a site is essential to ensuring a successful treatment outcome (Trumm, 2010; Trumm & Watts, 2010). Full-scale passive treatment systems need to be based on "AMD chemistry, flow rates, available land area, surface topography, and the results of small-scale field trials and laboratory experiments" (Trumm et al., 2006, pp 2154; Trumm & Watts, 2010). It is often difficult to achieve water quality requirements by using one system alone, so coupling is an option in many cases (Ziemkiewicz et al., 1996). Most passive treatment systems use one of two methods to improve water quality – either a reducing or an oxidizing strategy (Trumm et al., 2006; Trumm 2010).

Oxidizing systems work by continuing the natural Fe-oxidation process (Equation 1.2) and raising the pH to a suitable level to precipitate ferric hydroxide (Trumm, 2010). These systems require oxygen input to allow oxidation, so are well suited to sites with steep topography and work best with AMD with high DO and Fe in its oxidized form, Fe^{3+} (Trumm & Watts, 2010).

Reducing systems, however, reverse the oxidation process by reducing Fe and SO_4^{2-} and forming FeS_2, FeS, and H_2S, removing the former from the AMD stream (Trumm ,2010). These systems work best with AMD having low DO and Fe in its Fe^{2+} form (Trumm & Watts, 2010). Based on the AMD chemistry at Bellvue Mine described in Chapter 2, there was the opportunity to use either oxidizing systems by treating water from the cascade; or reducing systems by treating water from the pool (Trumm & Cavanagh, 2006). These two distinct AMD chemistry types are an interesting feature of the site, and allowed for the trialling of a range of passive treatment systems.

3.2.2. Sulphate–reducing Bioreactors

Several types of reducing systems have been developed over the years to address the in situ passive treatment of AMD, one of which is the sulphate-reducing bioreactor or SRBR (Trumm & Watts, 2010). This system operates by promoting the oxidation of organic carbon (CH_2O) to HCO_3^- and reducing SO_4^{2-} to H_2S(aq) in the following reaction (Behum et al., 2011):

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S\ (aq) \qquad \text{Equation 3.1}$$

The HCO_3^- then reacts with H^+, which decreases the acidity of the AMD in the system. H_2S dissolves in water and the ions become available to bond with metals such as Fe, Ni and Zn, all of which are found in the Bellvue AMD (Behum et al., 2011).The process is facilitated by microbial communities that develop in the substrate of the bioreactor, and are sustained by a complex carbon source which is commonly a mixture of plant materials (Hengen et al., 2014).

Bioreactors are one of the best-performing passive treatment options in terms of acidity reduction (Behum et al., 2011;Hengen et al., 2014), and are preferred to more traditional treatment types because they have higher metal removal rates at lower pH and generate waste sludge that is more stable than other systems (Neculita et al., 2008). Limestone is commonly used as the source of alkalinity in bioreactors, but alternatives like waste mussel shell can also be employed (Hengen et al., 2014; McCauley et al., 2009). Bioreactor performance can be limited by the severity of AMD chemistry and extremely high metal concentrations, hydraulic residence time, substrate clogging, and variations in flow (Mackenzie et al., 2011; Neculita et al., 2008).

3.2.3 Mussel Shell Reactors

Using mussel shell as an alkalinity source to treat AMD without being mixed with other substrates (as in a bioreactor) has not been as common in international literature as other types of systems. The mussel shell reactor technology is relatively new in New Zealand, which has an important mussel-farming industry, and the only existing field trial in the West Coast region prior to this research was carried out by Solid Energy at Stockton Coal Mine (Crombie et al., 2011). This system was designed to be even more simple and cost-effective than a bioreactor, and uses just a single treatment medium of mussel shell (although this is mainly made up of calcium carbonate, $CaCO_3$, protein and chitin) and the performance of the system at Solid Energy was successful enough to justify further installation of systems (Crombie et al., 2011).

The long-term performance of the mussel shell reactor may be compromised by the sludge build-up within the system that clogged the substrate and prevented homogenous flow (Crombie et al., 2011). The system at Stockton used a downflow design and an upflow design may have avoided this by forcing sludge away from the influent pipe thereby preventing clogging, and also stopping atmospheric oxygen at the top of the system reacting with the influent AMD.

Downflow is the more commonly-used technique, and involves piping AMD into the top of a treatment system. An effluent pipe is installed at the bottom of the system and this drains the treated AMD out of the system, using gravity to aid the flow. An upflow design pipes the AMD into the bottom of the system, and has an effluent pipe at the top. The AMD is forced up through the treatment substrate by the pressure of incoming AMD, and exits at the top. Upflow systems have the potential to be more reducing because the influent AMD enters an anoxic environment immediately, rather than being exposed to atmospheric oxygen which could start the oxidation process, like a downflow system.

3.2.4 Anoxic Limestone Drains

One of the most common types of reducing passive treatment system is an anoxic limestone drain or ALD (Hedin, et al., 1995; Skousen et al., 2000; Trumm et al., 2005). The limitations of these systems when treating oxidized Fe^{3+} and associated plugging and armouring of the

limestone are well documented in the literature (Ayora et al., 2013; Trumm, 2010; Ziemkiewicz et al., 1996; Ziemkiewicz et al., 1997); but ALD technology can be extremely effective when treating AMD with reduced Fe^{2+}. The ALD - a buried bed or pipe with no head space – is filled with limestone; this then reacts with the AMD and generates alkalinity via calcite dissolution (Ayora et al., 2013). Oxidation and precipitation of metal oxides takes place downstream of the ALD, preventing clogging and armouring of the limestone. This does however, require further downstream systems to accommodate this precipitation (Ayora et al., 2013).

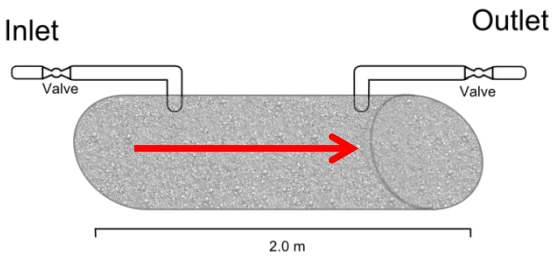

Figure 3.1. ALD design, showing the arrangement of the inlet and outlet pipes. The flow of AMD is demonstrated by the red arrow.

3.3 Passive Treatment at Bellvue

3.3.1. Initial Study

A 2006 study by Trumm and Cavanagh was undertaken as part of a training exercise by the West Coast Regional Council using Bellvue Mine as a case study for the investigation and selection process for AMD treatment. This involved geochemical sampling at the mine and use of results from that to determining the most appropriate treatment systems to install. The results of the 2006 study have been fundamental to the passive treatment selection process, and creation of sampling regimes for both the baseline geochemical surveying and treatment system monitoring that were carried out as part of the research programme described in this thesis.

Bellvue Mine AMD is characterized by high dissolved Fe and Al in particular, as well as elevated Mn, Zn, and Ni. pH is typically low (< 2.6 at most sites) and DO and conductivity change between the pool site at the top of the mine site and the bottom. This creates two main types of AMD at the site : type (I) low DO, low pH AMD with reduced Fe^{2+} at the pool site; and type (II) high DO, low pH AMD with oxidized Fe^{3+} at the bottom site. Passive treatment systems were installed at the mine based on literature research and previous field studies from the West Coast of the South Island. These were divided into two types:

- Three reducing systems treating type (I) AMD: a sulphate-reducing bioreactor with mussel shell as the alkalinity source; a mussel shell reactor, and an ALD system
- One oxidising system treating type (II) AMD: another mussel shell reactor sourcing AMD from the cascade with Fe in an oxidized form

These systems were installed at the site (Figure 3.2) and monitored on a weekly basis at first, followed by fortnightly monitoring. The aim of the treatment was to increase pH of the treated AMD and reduce the dissolved metal concentrations in the discharge by precipitating them as various sulphides (in the reducing systems) or oxides (in the oxidizing system).

Figure 3.2. Position of the treatment systems at Bellvue Mine. **(A)** View of all four systems, with the three reducing systems grouped in a red box. The oxidizing mussel shell reactor is on the left hand side. The ALD was obscured in this image, so the relative position has been indicated by the brown cylinder. **(B)** View of the three reducing systems, with the ALD running from left to right in the foreground. The flow of AMD in both images is from left to right and the discharge path is the orange stream in the background of each photo.

3.3.2. System Design and Installation

The bioreactor and two mussel shell reactors were designed according to similar systems put in place by Trumm et al., 2008. They consisted of a 1m^3 plastic composite intermediate bulk container or IBC, with the top removed and an average volume of 0.67 m^3. All three systems were upflow, with the AMD influent pipe running from the pool at the top of the slope and entering at the bottom of the IBC, then discharging at the top of the tank (Figure 3.3). The systems were each filled with 0.5 m^3 of treatment medium (mussel shell for the mussel shell reactors, and a mixture of materials for the bioreactor). Porosity measurements were made for each, and used to calculate the required flow rate to achieve a 24-hr hydraulic residence time (HRT). Once the systems had been installed in the field, the IBC's were filled with AMD and the system treatment monitoring commenced.

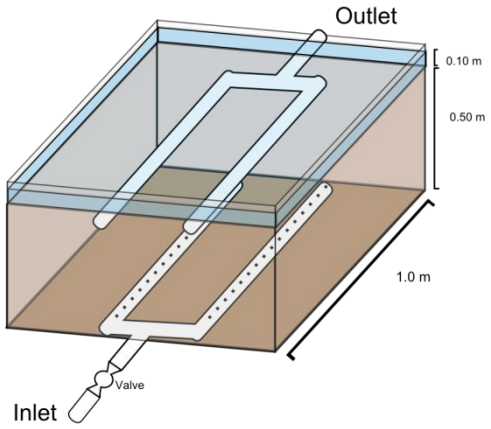

Figure 3.3. Diagram showing the design and layout of AMD pipes in the bioreactor and mussel shell systems. The influent pipe was at the bottom of the IBC and the water flowed up through the substrate, reacting with the treatment media, before flowing out the effluent pipe at the top of the IBC. The blue layer at the top denotes the 10 cm layer of standing water, while the brown layer is the treatment media.

The ALD was designed based on previous field trials conducted both overseas and in New Zealand, using the common design of a pipe filled with limestone. Once the pipe was in place at the site, it was filled with limestone and sealed at either end. It was then filled with AMD and the treatment monitoring began. Detailed descriptions of each system are given in the following sections.

3.3.3. Bioreactor and mussel shell reactors

The bioreactor system was based on a smaller-scale bioreactor being trialled at the University of Canterbury (Uster et al., 2013). It was composed of 30% crushed fresh mussel

shell (Figure 3.4 (A)), 30% bark chips, 20% bark mulch, and 20% regular garden compost (Figure 3.4 (B)). This was mixed to create a homogenous substrate (Figure 3.4 (C)) before being placed into the bioreactor IBC. The substrate was not compacted and had 40% porosity, which was calculated by filling a bucket of known volume with the bioreactor mix and saturating it with water, before draining the bucket and measuring the volume of water that was collected.

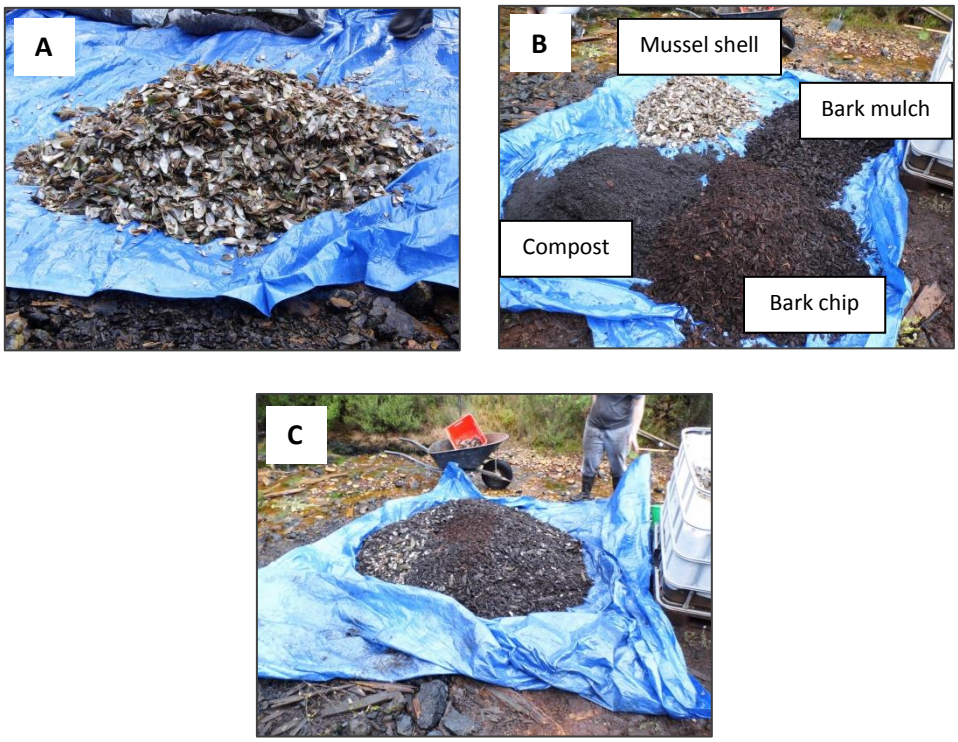

Figure 3.4. Treatment media used in the bioreactor installed at Bellvue Mine. (A) Mussel shell: around 3 weeks old, high organic content, semi-crushed. (B) Mix of mussel shell, bark mulch, bark chips, and garden compost that were used in the bioreactor. (C) The bioreactor treatment media after all of (B) had been mixed to create a homogenous substrate.

Both the bioreactor and mussel shell systems were designed to have AMD upflow within the treatment substrate. The AMD was gravity-fed from the pool at the top of the site into the bioreactor, and the reducing mussel shell reactor (the MSR) via 25 mm alkathene piping. This was interrupted by a timer valve which was set to open at regular intervals, slowing the flow rate into the systems and allowing for a 24-hr HRT. The timer valve fed into a splitter pipe (Figure 3.5), which was drained by two smaller pipes – one side led to the bioreactor,

the other to the MSR. The timing for the valve was established in a series of calculations that took into account the required flow for each system, the available flow from the pool, the volume of the splitter pipe, and the time it took to fill the pipe and drain into the systems.

40 mm PVC piping was used for the influent flow into each system, and laid out on the bottom of each IBC in a pattern that would allow for even dispersion of the AMD through the substrate (Figure 3.6). The AMD flowed up through the mix and out via another section 40 mm PVC pipe that mirrored the arrangement of the inflow pipe, then out the other side of the tank via a section of 25 mm alkathene that also doubled as the system sampling point.

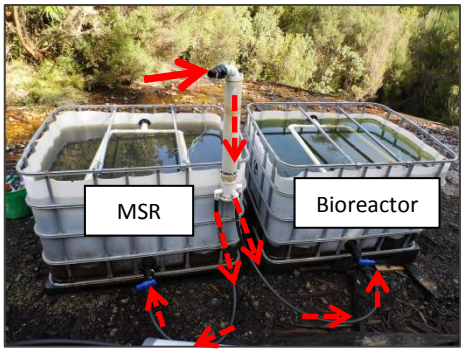

Figure 3.5. View of the splitter pipe between the MSR and the bioreactor. The pipe was filled with AMD from the pool by a timer valve, and the flow was then split evenly between the two systems (shown by red arrows).

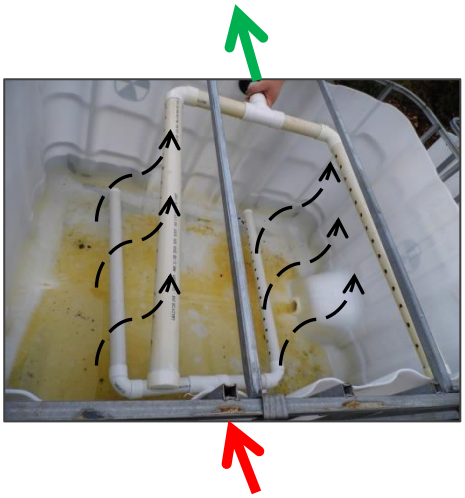

Figure 3.6. Overhead view looking down into the (empty) bioreactor treatment system. AMD inflow is indicated by the red arrow, and the effluent discharge point is indicated by the green arrow. The mussel shell reactors had the same design.

A 0.1 m head space of standing water was left between the top of the substrate and the effluent pipe in each system. This prevented Fe and other metal precipitates from clogging the effluent pipe.

The mussel shell reactors were separated into two types, one (the MSR) treating the type (I) Bellvue chemistry. The second mussel shell reactor (the MSO) was treating type (II) Bellvue chemistry. The MSR was the reactor that was connected to the splitter pipe along with the Bioreactor and treating reduced AMD from the pool. Both systems had the same design as the bioreactor, including the layout of influent and effluent pipes, HRT (all had a 24-hr HRT), and substrate thickness and headspace depth (0.5 m and 0.1 m respectively)

The MSO was fed by an independent source of AMD, being from the cascade rather than the pool. This was collected using a custom-made cistern (Figure 3.7) located at site C that drained down to another timer valve. This was set to open at half the rate of the other timer valve because unlike that, this was only feeding one system and so only needed half the flow to maintain a 24-hr HRT.

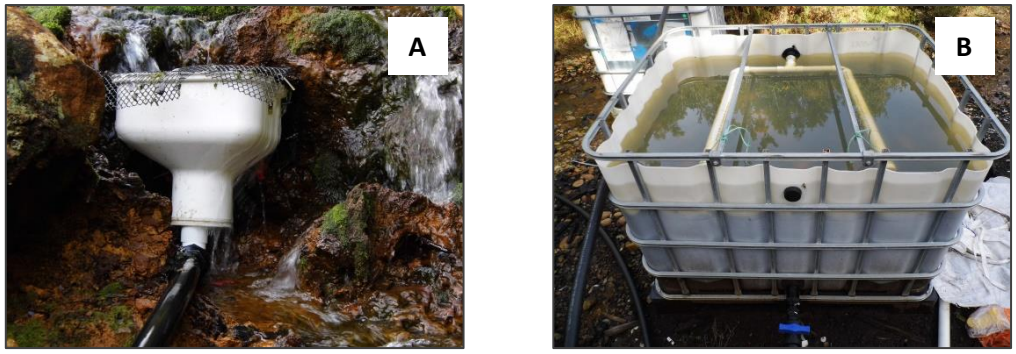

Figure 3.7. (A) The cistern at site C, that collected oxidized AMD for the MSO treatment system. The AMD flowed in the top of the cistern and large detritus (leaves, sticks etc.) were blocked by a layer of gutter screen. The outlet at the bottom connected to the black alkathene pipe that flowed into the timer valve and the MSO. **(B)** View of the MSO, with the inflow pipe at the bottom centre of the image. The timer valve controlling the flow was just out sight – the blue tap visible was a ball valve acting as an emergency shutoff valve.

3.3.4. ALD System Setup

The ALD design was based on previous works, both international and within New Zealand. It consisted of a 2 m-long PVC pipe, filled with limestone and sealed at each end. The influent AMD flowed in the bottom of the pipe, and the effluent AMD flowed out the top end of the pipe (Figure 3.8). The ALD was also tilted, so that the effluent end was higher than the influent. This was because it was essential that the ALD was treating reduced AMD only, and

the DO content was as low as possible. By tilting the pipe, any oxygen trapped in either the ALD or the 25 mm alkathene pipe leading from the pool to the inflow, would then collect at the effluent end of the ALD and be expelled as the water filled the pipe. Carbon dioxide produced by calcite dissolution in the ALD would also pressurize the system and expel any remaining oxygen. To ensure no new oxygen was getting into the system, all joints were tightly sealed and there was an uninterrupted supply of AMD from the pool to the inflow. Treatment samples were collected at the effluent end.

Figure 3.8. ALD with influent pipe at the top right of the picture. Effluent AMD flowed out at the bottom left of the image. Flow was directly from the pool, with no opportunity for oxygen to be introduced, and controlled by two ball valves at the top of the cascade.

3.4. Treatment System Sampling Regime

Based on the recommendations made in Trumm and Cavanagh (2006), the systems were filled with AMD and the bio- and mussel shell reactors were then left for 2 weeks to allow microbial populations essential to the treatment process to populate the substrate. Weekly sampling of pre-defined parameters was undertaken. For each system, in-field water quality measurements of pH, EC, temperature, and DO were taken using the same PSI probe as for the baseline chemistry sampling; and water chemistry samples were collected for analysis by Hills Laboratories. The influent chemistry was sampled for the same parameters, at the same time. Because the AMD came direct from either the pool or mid cascade sites, AMD from these sites was used as a proxy for the influent AMD chemistry in the systems.

Sampling protocols for the water quality monitoring were the same as for the baseline chemistry surveys, and the probe was submerged in the standing water at the top of each treatment system and allowed to settle before a reading was taken.

For the water chemistry sampling, the same protocols and bottles were used for dissolved metal concentrations because the same five key metals (Fe, Al, Mn, Zn, and Ni) were being

monitored. In place of the 100 ml light blue unfiltered, unpreserved sample collected for sulphate and alkalinity analyses, a 1 L bottle of unfiltered, unpreserved sample was taken. This covered not only sulphate and alkalinity, but also total ammoniacal nitrate, nitrite-N, nitrate-N, nitrite-N + nitrate-N, and total reactive phosphorus were also measured. A separate 250 ml unfiltered sample was collected in an amber glass container for analysis of dissolved organic carbon (DOC), although this was only for the reactors (bio and mussel shell). The ALD did not have a carbon-based substrate, so there was no need to monitor the C-flux through the system as closely. The sampling regime for site A (the source of AMD for the bioreactor, MSR, and ALD) and site C (the source of AMD for the MSO) was sampled using the sample protocols and methods as the treatment systems.

Flow rates from each system were monitored using a 1 L graduated cylinder and stopwatch. Flow was measured three times and averaged to determine flow rate. This was a measure of how effectively the timer valve controlling AMD inflow was working. Unfortunately this was the hardest system parameter to control, and it was often the case that the flow between systems was uneven, and there were issues with flow that was either too fast or too slow throughout the sampling period. This has important implications for the results of the system treatments, as discussed in Chapter 4.

3.5 Treatment System Results

3.5.1. Sampling Protocols

Four treatment systems operated at Bellvue Mine for a period of four months. The treated discharge from each system was sampled and the results are displayed in the following sections. Overall, there was a noticeable decrease in dissolved metal concentrations and a marked increase in pH from all systems except the ALD.

A summary of the averaged percentage removal rates for the main chemical parameters monitored for each of the systems are displayed in Table 3.1. These were calculated by averaging the results measured for the system and its source, i.e. for the bioreactor, MSR, and ALD this was site A; and for the MSO this was site C. The difference between the system and its source was the percentage remaining in solution, so the inverse of this was the percentage that had been removed by treatment.

Removal rates in black indicate a positive percentage removal rate, meaning the concentration of the metals or other geochemical properties in the discharge from the systems has decreased compared to the incoming source.

Removal rates in red indicate a negative percentage removal, or an increasing concentration of metals in the discharge compared to the AMD from the pool.

The percentage removal rates for the ALD are nearly all negative. This treatment system did not decrease the concentration of metals, among other things, in the discharge from Bellvue Mine, but instead increased it for all of them. This is likely due to mechanical problems and equipment failures with this system. The concentration of Ca in the treated AMD is higher for all four systems compared to the inlet, but this it to be expected given the treatment media in all systems was some variation of a calcium-based product, either mussel shell or limestone rock.

Table 3.1. Summary of the averaged percentage removal rates of various chemical parameters measured for each of the four operating passive treatment systems at Bellvue Mine. Red indicates negative removal. Black indicates positive removal.
(*) indicates parameters that were not measured at the source of the AMD for the MSO (site C), and as such no percentage removal rates can be calculated.

Chemical Parameters	MSO	MSR	Bioreactor	ALD
Dissolved Metals (g/m^3)				
Fe	99.8	60	69	-9
Al	99.98	86	86	-20
Ca	-485	-329	-348	-75
Mn	51	-6	-44	-28
Zn	98	66	68	-38
Ni	99	55	49	-26
Sulphate	43	-3	-12	-18
in-field pH [lab result]	-177.19	-151	-123	-9
Electrical Conductivity	11	15	21	-3
Dissolved %	64	-32	-220	-284
Oxygen mg/L	67	-21	-188	-269
Acidity	*	82	88	-89
Alkalinity (g/m^3 as $CaCO_3$)	*	-3673	-1358	65
Bicarbonate	*	-10767	-5767	0
Nitrite-N	*	25	60	6
Nitrate-N	*	26	71	40
Nitrite + Nitrate	*	24	66	39
Total Ammoniacal-N	*	-2233	-370	-33
Total Reactive Phosphorus	*	0	0	0
DOC	*	-52	-4	19

3.5.2. Mussel shell oxidised (MSO)

The results from the MSO passive treatment system that was installed at the site are shown in Figure 3.9 below. This system decreased all of the major metal contaminants in the Bellvue Mine AMD over the four-month sampling period, apart from Mn (Fig. 3.9 (A)). Mn increased after 19 November in a trend that did not correspond with any of the other metals. Zn in particular showed a 98% decrease in concentration over the sampling period, and the MSO was the only treatment system to have a constant decrease in Zn over the treatment period (Fig. 3.9 (B)). Dissolved Fe concentration spiked at the end of October before recovering over the course of two weeks to a former level. The reasons for this spike are unknown at this point.

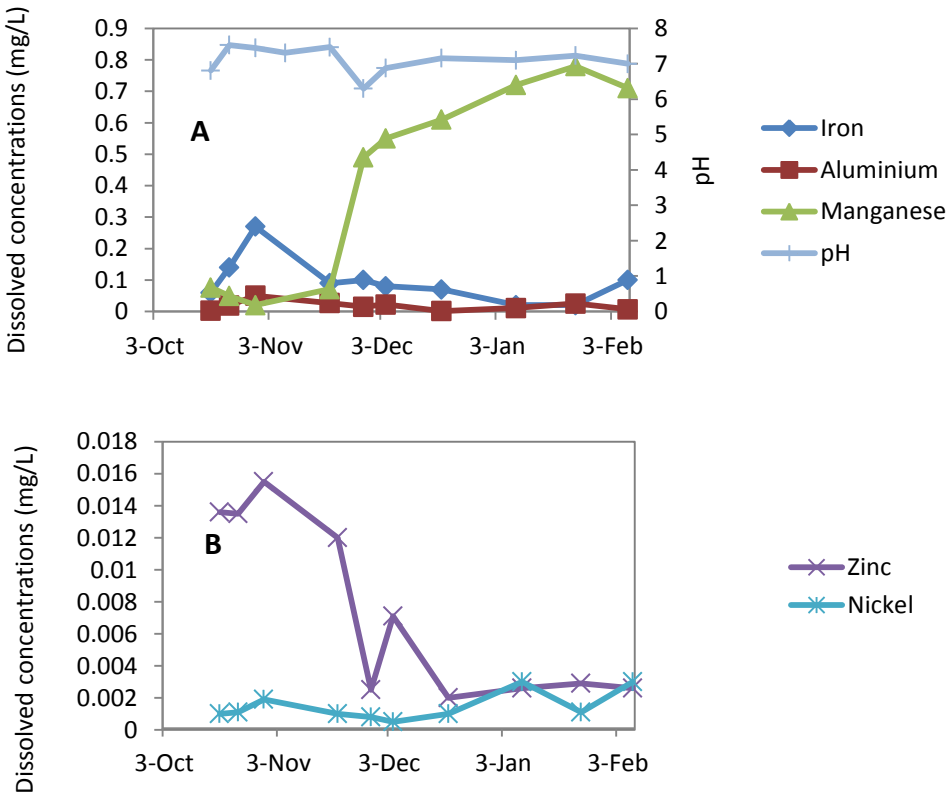

Figure 3.9. Dissolved metal concentrations in treated AMD discharging from the MSO reactor at Bellvue Mine. (A) pH was consistently neutral and Mn increased over the treatment period

Fe, Al, and Zn showed the most impressive decreases over the trial, particularly the dissolved Al concentration which decreased by five orders of magnitude after treatment by the MSO.

3.5.3. Mussel shell reduced (MSR)

This system was identical in design to the MSO, but treating water direct from the pool with a much lower DO content and Fe still in a reduced form (Fe^{2+}). The dissolved metal concentrations in the discharge from this system are shown in Figure 3.10.

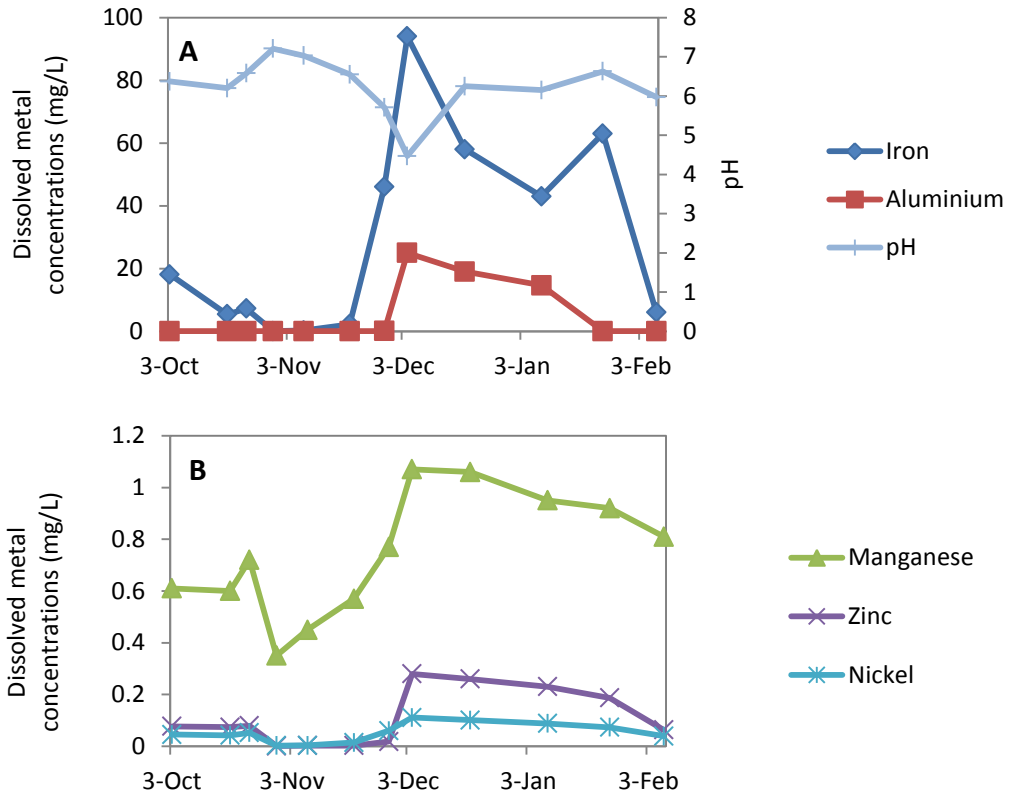

Figure 3.10. Dissolved metal concentrations of the discharge from the MSR treatment system at Bellvue Mine. **(A)** dissolved Fe and Al; and **(B)** dissolved Mn, Zn, and Ni concentrations. pH was generally consistent, although there was a small decease on 3 Dec.

This system showed an interesting pattern because all metal concentrations (except Fe) did not change for the first two weeks from the start of the sampling period. A slight increase in pH (from 6.2 to 7.2) throughout October was accompanied by a decrease in all dissolved metal concentrations. The concentration of these metals in the discharge from the MSR peaked on Dec 4, at which point the pH was the lowest on record. As pH recovered and increased from that point onwards, the metal concentrations decreased. The reason for this drop in pH and spike in metals, in particular Fe and Al, is speculated to have been caused by an operational failure with the flow into the system, which is discussed more in Chapter 4. Overall, there was a 2-fold difference in concentration magnitude between (A) dissolved Fe

and Al; and (B) dissolved Mn, Zn, and Ni concentrations, which is not surprising because the former are found in higher concentrations in the influent AMD.

3.5.4. Bioreactor

Metal concentrations in the discharge from this system fluctuated, as shown in Figure 3.11. Fe in particular varied over a wide range from 0 to 70 mg/L, and towards the end of the sampling period the level of dissolved Fe^{2+} in the treated AMD coming from the bioreactor increased markedly, before decreasing in the last recorded sample (Figure 3.11 (A)). Al also peaked near the end of the sampling period, but overall the concentration levels were more consistent throughout the testing period compared to Fe.

Dissolved Zn and Ni were consistently discharged at very low concentrations (<0.2 mg/L), while Mn was higher (between 1.4 and 0.58 mg/L) (Figure 3.11 (B)). The curve of the Mn trend follows the pH closer than any of the other metals measured in the discharge.

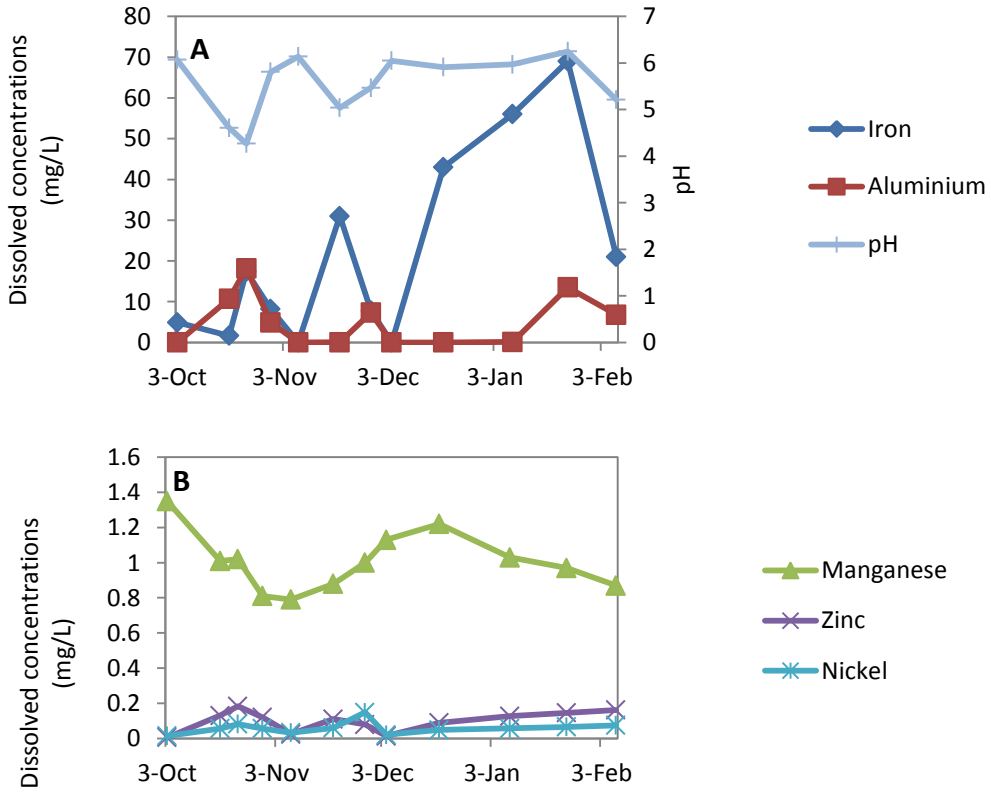

Figure 3.11. (A) Dissolved Fe and Al concentrations in treated AMD discharging from the bioreactor at Bellvue Mine, compared to pH. **(B)** Dissolved Mn, Zn, and Ni concentrations. Note the difference in scale of the dissolved concentrations (y-axis) between (A) and (B). This is because Mn, Zn, and Ni occurred in much lower concentrations than Fe and Al.

3.5.5. Anoxic Limestone Drain (ALD)

For the ALD to be considered to function effectively, the AMD treated by this system needed to be attaining a pH of 4.0 (measured at the discharge) before it could be processed by downstream treatment systems (these are not discussed in this report because they did not operation during the report period). As shown in Figure 3.12, the pH discharging from the ALD was never higher than 3.2, and for most of the sampling period was similar to the pH of its source water (the pool site). The high dissolved metal concentrations in the AMD from the pool were maintained throughout treatment by the ALD, and in most cases were even increased. The correct flow rate through the system was not initially established because the caps sealing the ALD tube failed and in the fortnight that it took to repair them, the ALD sat inactive and full of acidic AMD from the pool. It is hypothesized that this caused armouring of the limestone by Fe-precipitates, which is discussed further in Chapter 4. The results from the ALD treatment are displayed below.

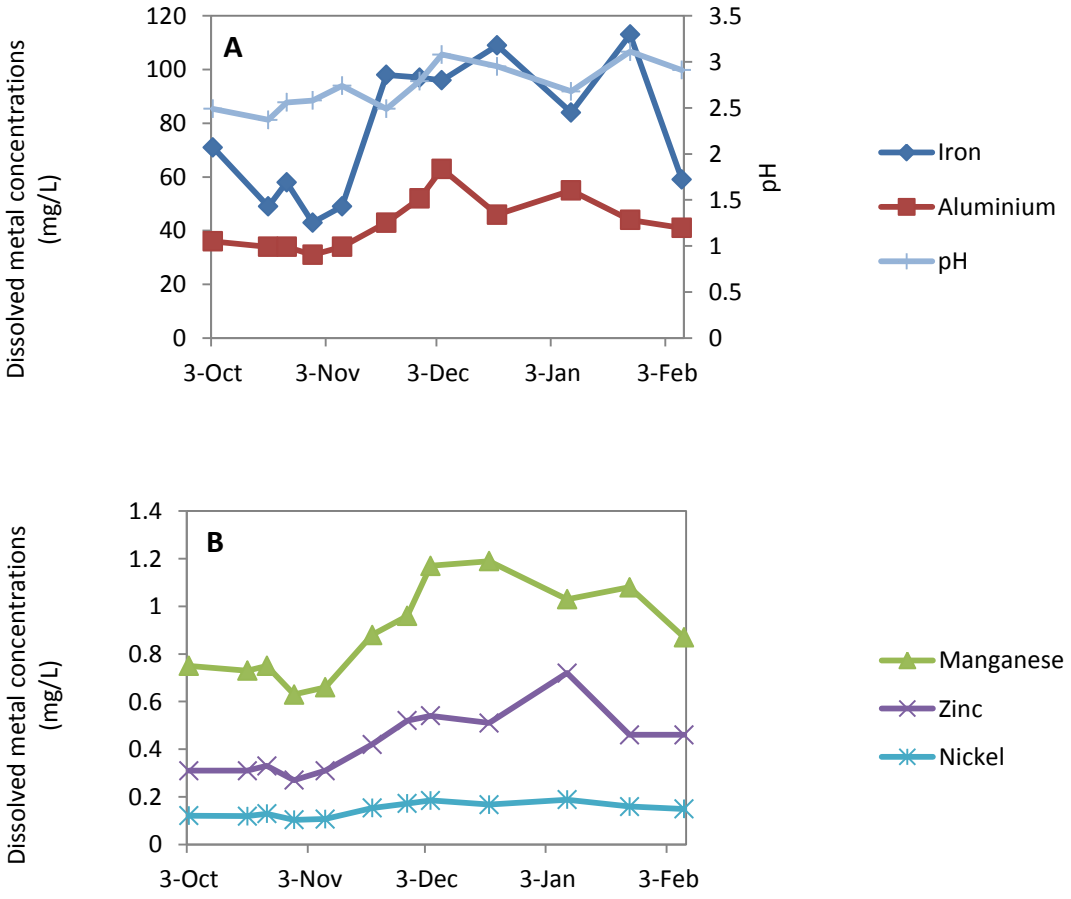

Figure 3.12. (A) Dissolved Fe and Al concentrations in Bellvue Mine AMD from the ALD treatment system. **(B)** Dissolved Mn, Zn, and Ni concentrations. Over time Mn concentrations (in green) increased, as did Zn (in purple); while Ni (in blue) was relatively similar.

There was no net decrease in any of the metals from the ALD, and each metal became more concentrated in the discharge between October 31 and November 7. This is potentially the effect of seasonal trends in influent AMD chemistry. The warmer months were marked by increasing metal concentrations in the mine discharge, as was discussed in Chapter 2. From November 7 most metals started to decrease in concentration, in particular Fe decreased to 60 mg/L, but they did not return to their pre-summer levels.

3.6. Summary of Passive Treatment Trials

The chemistry and existing conditions at Bellvue make this site well suited to passive treatment, and when using AMD from the pool site, reducing passive systems are the best options for effective treatment.

Based on the recommendations made in Trumm and Cavanagh (2006), and ALD, two mussel shell reactor and one sulphate-reducing bioreactor were installed at the site. The chemistry of the treated discharge from these systems was monitored for a 4-month period.

The passive treatment systems installed at the site proved effective at removing both metals and sulphate from the Bellvue Mine AMD being fed into the treatment systems. The results from the various passive treatment systems showed constant variation in both chemistry and hydraulic residence time. In general, the two Mussel Shell reactors and the Bioreactor all reduced the concentration of dissolved metals in the AMD by around 60 to 99%, while dissolved metals from the ALD increased in concentration for the majority of the study.

4. Remediation Issues and Options

4.1. Introduction

The objectives of the study conducted at Bellvue were to:

A) Increase the database and understanding of the background AMD chemistry of the mine discharge by conducting a 12- month baseline survey of the mine discharge and the changes to the receiving waterway (Cannel Creek) after the AMD enters.
B) Trial a range of small-scale passive treatment systems with the aim of making recommendations for the most effective type of system to use at Bellvue and other sites with similar geochemistry.

With this in mind, determining the best type of system to install at a site like Bellvue is not straightforward. There are many factors that influence the performance of a treatment system and many ways that it can be measured. One such method is by using a comparison of how efficient the system was in terms of decreased dissolved metal concentrations and increased pH compared to hydraulic residence time (HRT). Other methods include calculating metal and acidity loading rates per day, and this type of analysis is useful for determining the total volume of treated water and the amount of contaminants that have been removed, as well as the life expectancy of a system.

This chapter will discuss the performance of the four systems trialled at Bellvue Mine. The performance analysis will be used to make comparisons of the efficiency of each system individually as well as between the different types. This takes into account the limitations and issues that each passive treatment system was affected by.

4.2. Hydraulic Residence Time (HRT) Analyses

There was a large amount of flow variability within the reduced passive treatment systems (the MSR and bioreactor) and between these and the oxidized passive treatment system

(the MSO). This made it difficult to analyse the effectiveness of each system and make comparisons of their performance on an individual level. When the HRT for each system was normalised and compared to % removal of Fe (Figure 4.1), all three systems performed to a similar standard. The target HRT for the three reactor systems was 24hrs, and this had come from existing literature and previous field trials. The HRT for the ALD was unspecified, and the aim for this system was to achieve pH 4 at the effluent, so the flow was designed to be easily adjusted to make achieving this easier.

The bioreactor was more effective than the MSR because at the 24hr HRT it was consistently removing more Fe, on average. The MSO had less flow data measurements taken and so despite the consistently high Fe removal, there is less confidence in the system performance overall. However, it was still performing as well as both the MSR and bioreactor at the 24hr HRT, and outperforming them at higher residence times.

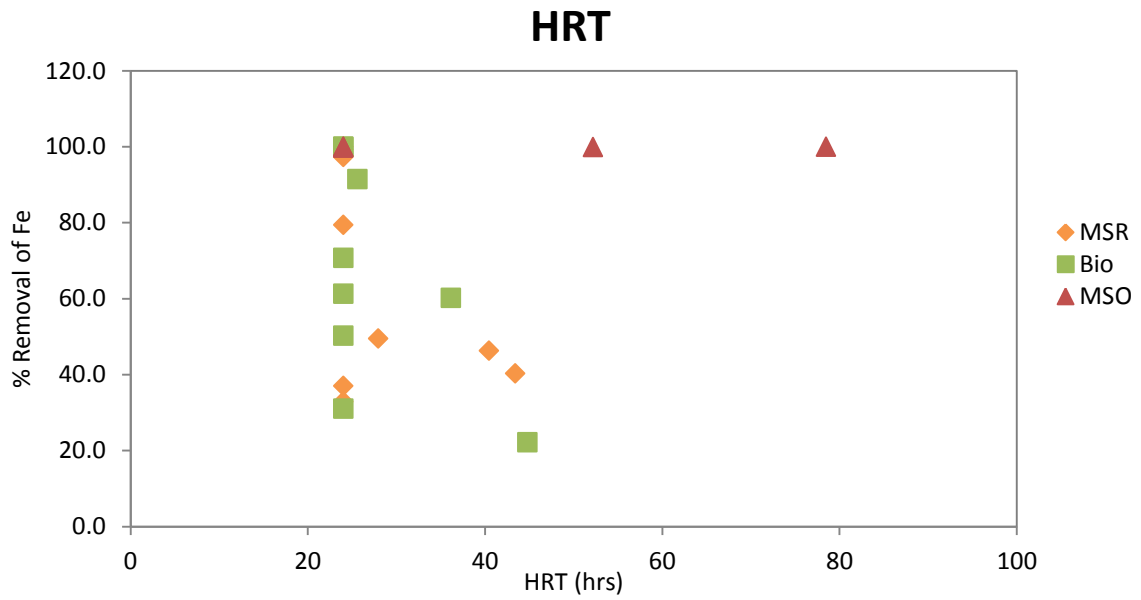

Figure 4.1. Summary results showing the variation in HRT for the MSO (red triangle), MSR (orange diamond) and the bioreactor (green square); and the corresponding percentage removal of Fe.

By comparing the dissolved metal concentrations discharging from each system (Figure 4.2) at certain hydraulic residence times, as opposed to comparing them over the sampling period, it is easier to visualize the performance of the systems.

Comparing the performance of the two reducing passive treatment systems (the bioreactor and the MSR) shows that for Fe, initially the Bioreactor was the fastest at decreasing concentrations to low levels, while the MSR only had reduced levels (less than 50 mg/L) once residence times reached over 30 hours.

At the 30 hr HRT, the pattern of dissolved Fe concentration changed between the two systems (HRT <30 hrs had up to this point been similar) (Figure 4.2 (A) and (B)). The concentration of Fe in the bioreactor increased sharply after 25 hrs, while it continued to decease in the MSR. Dissolved Al levels were similar for both of these systems, as were Mn, Zn, and Ni. Mn is always more concentrated in the treated discharge, especially for the bioreactor, but concentrations of Zn and Ni are very low (<0.3 mg/L) for both systems.

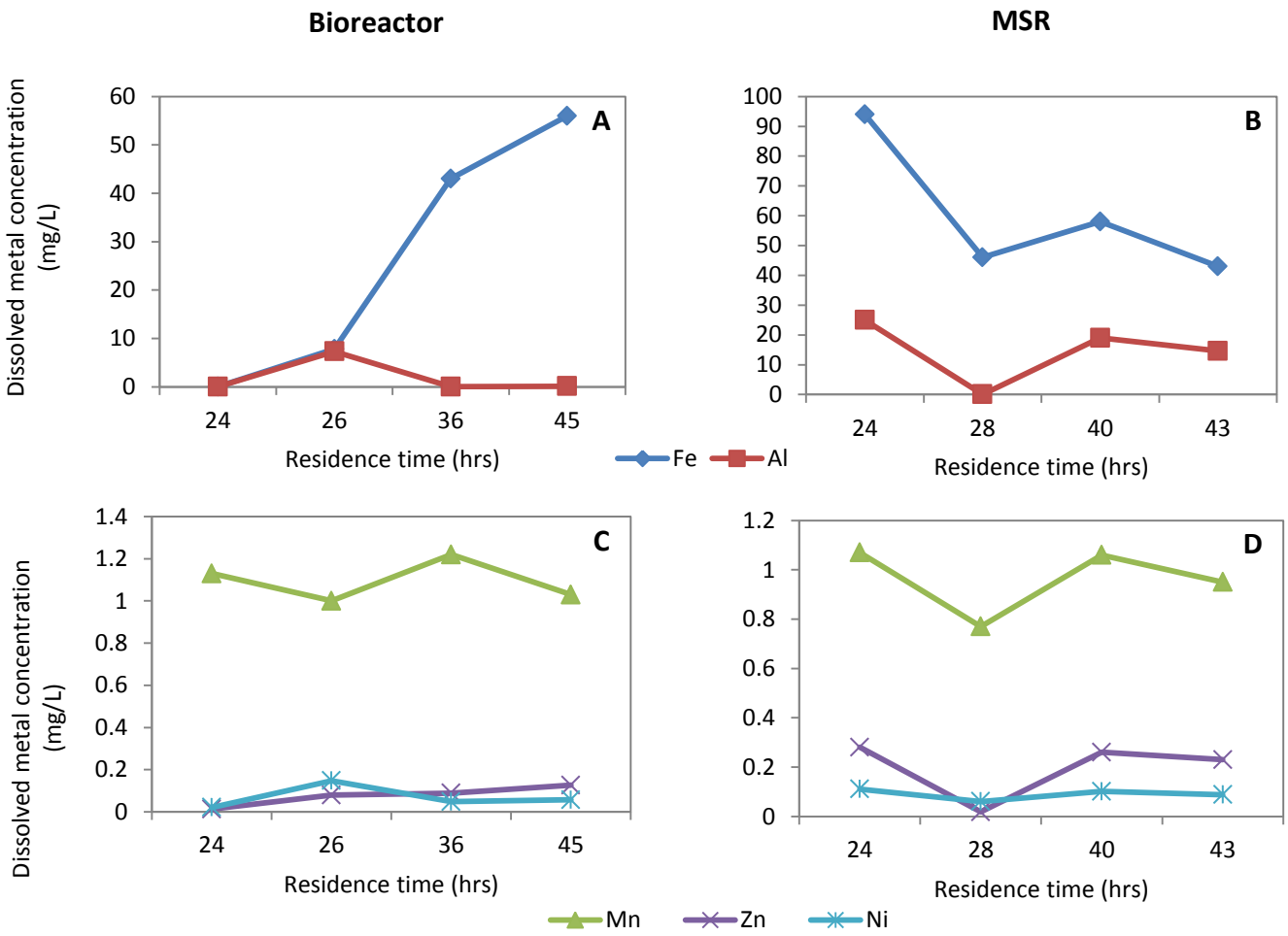

Figure 4.2. Dissolved metal concentrations from reducing passive treatment systems at specific hydraulic residence times. **(A)** Dissolved Fe and Al from the bioreactor system. **(B)** Dissolved Fe and Al from the MSR. **(C)** Dissolved Mn (green), Zn (purple), and Ni (blue) concentrations from the bioreactor system and **(D)** from the MSR system.

Comparing the two mussel shell reactors (MSR and MSO, Figure 4.3) shows that the MSO reduced the concentration of Fe and Al to very low levels (below 0.1 mg/L), but that this occurred at longer residence times than for the MSR. The MSR at its longest residence time was only just approaching the shortest residence time of the MSO, and yet the iron concentration was still much higher than the MSO. A similar pattern was repeated for dissolved Al. The likely cause of this is because the MSO is treating oxidized AMD, which means the metals are already oxidized and more readily form precipitates. However, this implies that the MSO is being filled with metal precipitates quicker than the MSR, which could mean it will not have the same life expectancy as the MSR.

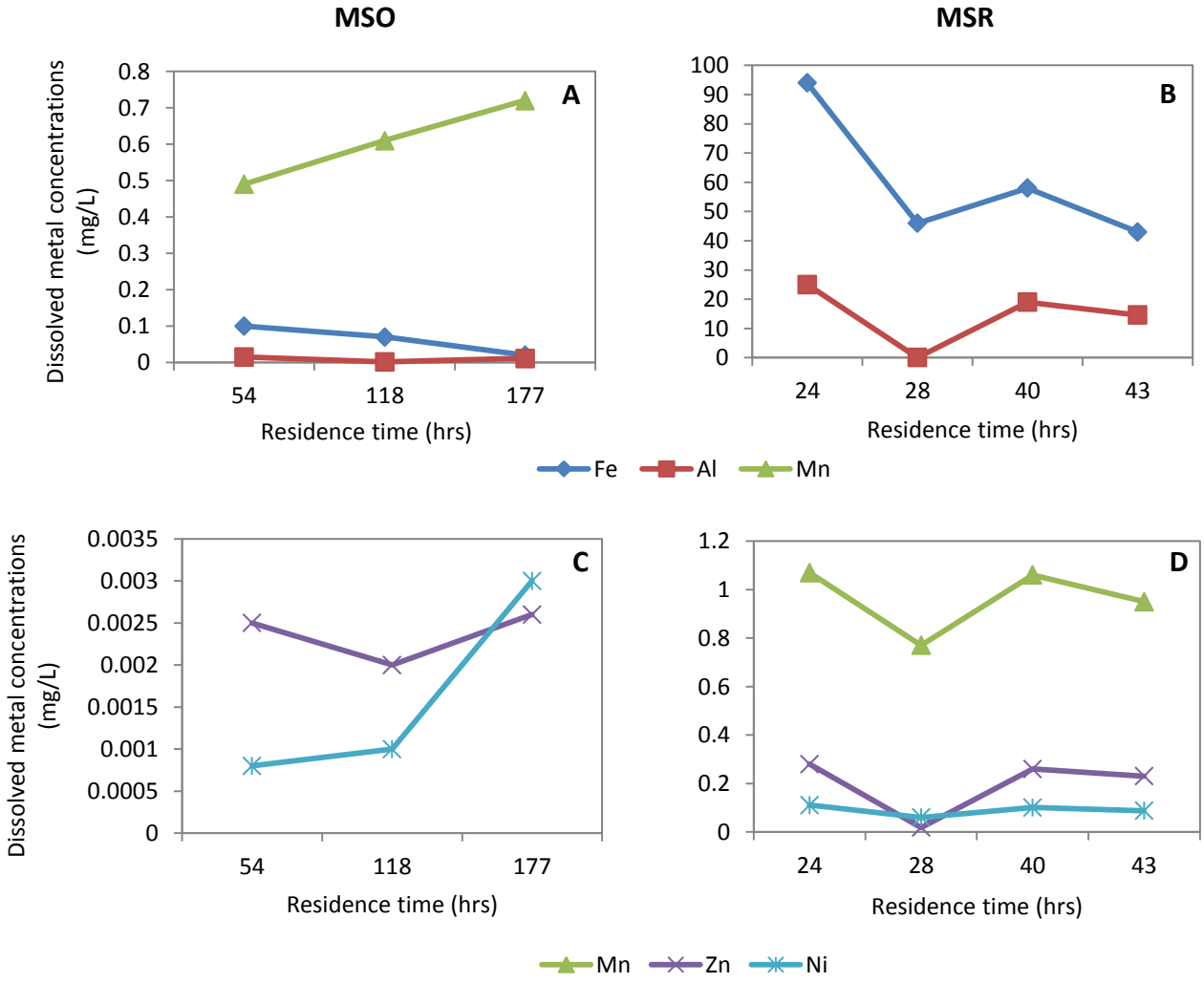

Figure 4.3. Dissolved metal concentrations measured at specific HRT's for the MSR and MSO passive treatment systems. **(A)** Dissolved Fe, Al, and Mn from the MSO. **(B)** Dissolved Fe and Al in the MSR discharge. **(C)** and **(D)** Dissolved Zn, Ni , and for the MSR, Mn (in green) concentrations in discharge from mussel shell reactors. There was no definitive trend for these metals.

Both Fe and Al were at very low concentrations in the MSO discharge, but Mn was 5 to 7 times higher. The concentrations of Zn and Ni were 1 to 2 magnitudes higher in the MSR compared to the MSO, but the residence time for the former was around half that of the MSO. These two metals did not reduce much after 40hrs residence time, and this could be because the pH for the MSR did not go as high as it did in the MSO (Figures 3.9 and 3.10) which could be limiting the speed and number of reactions taking place in the MSR.

Comparison of all three reactors is complicated by the variability they had in effluent dissolved metal concentrations; but overall they all performed to a high standard and removed over 50% of the metals in the AMD. The MSO performed extremely well, removing up to 99% of Fe, Al, Zn, and Ni (Table 3.1), which is attributed to the much longer residence time it had. Each system had strengths and weaknesses, and these will be important when scaling them up for full treatment programs.

4.2.1. Treatment System Performance

- The treatment systems that were operational throughout the trial period had varying degrees of effectiveness at decreasing dissolved metal concentrations and sulphate levels and increasing the pH of AMD from Bellvue Mine.

- The MSO had positive percentage removal of all five metal contaminants (Fe, Al, Mn, Zn, and Ni) as well as sulphate. This system performed exceptionally well in terms of the Fe and Al percentage removal rates, with nearly 100% of both removed, on average, from the AMD.

- The MSR did not perform as well compared to the MSO, but it still removed over 50% of four of the main metal contaminants. There was a 6% increase in manganese in the discharge from this system, and a 3% increase in sulphate.

- The Bioreactor also showed net increase in both manganese and sulphate, but on a larger scale than the MSR. Despite performing worse than both the MSO and MSR on these two parameters, it performed as well as, or better than, the MSR for percentage removal of Fe, Al, Zn, and Ni.

4.3. Mussel Shell Reactors

These systems were the easiest to install, required the least costly materials, and performed better than the other systems in terms of percentage removal of metals, sulphate, and conductivity. The percentage increase in alkalinity, pH, dissolved Ca, DOC, and bicarbonate from the mussel shell reactors (where measured) was also higher than the Bioreactor or ALD.

The long-term performance of the mussel shell reactors could be compromised by sludge build-up within the system, which clogs the substrate and prevents homogenous flow as seen in the mussel shell system at Stockton (Crombie et al., 2011). This used a downflow design, whereas the upflow design used at Bellvue may have avoided this by forcing sludge away from the influent pipe and preventing clogging. It would also stop atmospheric oxygen at the top of the system reacting with the influent AMD.

4.3.1. Mussel Shell Oxidized (MSO)

The MSO outperformed both the MSR and the Bioreactor in terms of percentage removal of dissolved metals, conductivity, and sulphate. It reduced Fe, Al, Zn, and Ni by 97-99%, compared to the MSR and bioreactor which only managed maximum removal percentages of 86% each.

It was also the most reducing system, with a net DO percentage removal of 64%, compared to the MSR and Bioreactor, which both showed a net increase in percentage of DO. The MSO's superior results are very likely the result of the much longer residence time, and the clear benefits of cycling the AMD through this system at half the rate of the other two (MSR and Bioreactor) can be seen. This could be because a longer residence time gives the SRB's more time to reduce sulphate to sulphide and precipitate in the systems. However, it will also create a faster build-up of sludge from the precipitates than the other treatment systems.

Compared to another mussel shell system treating oxidized AMD, the MSO performed to a similar level. The mussel shell reactor installed at Stockton Mine (Crombie et al., 2011) had an average HRT of 7.2 days (calculated from reactor volume and flow rate) compared to the

average for the MSO (5.9 days Appendix II). The Stockton reactor also achieved extremely high percentage metal removal rates, with 96-100% removal of Fe, Al, Zn, and Ni. This indicates that the MSR installed at Bellvue, despite being small-scale, was performing to the standards set by a full-scale system treating AMD of a similar chemistry.

4.3.2. Mussel Shell Reduced (MSR)

The MSR reduced more than fifty percent of the total metal load over the sample period, with the exception of Mn, which had a net increase in concentration. It was most effective at removing dissolved Al, followed by Zn, Fe, and Ni respectively.

Both the MSR and the Bioreactor had a net increase in sulphate levels following treatment, which is not an expected result or an ideal one, because sulphate is one of the key indicators of AMD contamination and so treatment systems should be reducing sulphate levels. The MSO did not have this sulphate increase, and there are multiple reasons why this may be the case:

1. The MSO had twice the HRT of the MSR and Bioreactor, but it was also treating water that was more oxidized and had travelled partway down the cascade, as opposed to being sourced directly from the pool. This means that metals were in a different form and more readily oxidized in the MSO. When HRT is normalized to 24 hrs the MSO still performs better than MSR, removing a higher percentage of dissolved metals and sulphate.

2. In regards to other geochemical parameters, the MSR was still effective at treating AMD because it increased pH and alkalinity substantially (> 150% for pH and more than 3000% for alkalinity) , and decreased acidity and electrical conductivity. All of these will make the treated discharge less likely to negatively impact the aquatic biota of the receiving waters.

3. The amount of DOC in the MSR discharge also increased by more than half. This is important because carbon is essential to organisms like sulphate-reducing bacteria, which exist naturally in waterways. These bacteria could potentially benefit from a greater availability of carbon and be able to reduce a greater volume of sulphate in

the creek, indirectly improving water quality downstream of the discharge point. This effect was not noticeable during the field trial given the scale of the systems operating at the site. However, this may be an important effect if a larger, full-scale MSR is installed that also has a net increase in DOC in the treated discharge.

4.4. Bioreactor

This system performed as well as the MSR in terms of metal removal and increases to pH. There was a 6% lower removal rate of Ni from the Bioreactor than the MSR. The dissolved metal concentrations measured in the discharge fluctuated over the entire sampling period, and this did not correspond with any seasonal periods. This effect was likely caused by the variation in flow rate through the reactor, but it is difficult to confirm this based on the sampling schedule which started at weekly intervals, then moved to fortnightly.

The period from December 5 2013 to January 30 2014 was marked by a significant increase in the concentration of dissolved Fe from the Bioreactor, indicating it was not functioning as efficiently as it had been previously. What is interesting is that by February 6, the Fe^{2+} concentration had reduced markedly, showing that the reactor was capable of recovering and improving its performance. HRT was the likely influence in this case. By this point, the sampling was occurring on a fortnightly basis, which only allows for a snapshot of the chemical environment, so any observations must take this into account.

The pH of the Bioreactor also fluctuated over the sampling period, and this likely affected the metal concentration of the system. Of all the metals measured, Mn most closely followed the pH in terms of fluctuations, which could indicate that it is more susceptible to pH in this reactor. The bioreactor was more effective at metal removal and pH increase than the MSR and ALD. It also increased alkalinity, although not as much as the MSR, and showed that a sulphate-reducing bioreactor is a viable passive treatment option for the Bellvue site, or others like it.

There have been multiple studies of bioreactors in New Zealand conditions. Those of note, that used mussel shell as the alkalinity source in the substrate, were the systems used by McCauley et al., (2009, 2010) and Mackenzie et al. (2011). Both studies found the highest

metal removal rates were for Al, Fe, Zn, and Ni, which closely matches the results for the bioreactor from this study. Another similarity between the Bellvue bioreactor and previous studies is the release of Mn from the reactor substrate. Mackenzie et al. (2011) measured a range of HRT's , and at low residence times (10hrs) 8.3% Mn was exported, while in the 2009 study by McCauley et al. there was an average export of 20.8% Mn.

Behum et al. (2011) and Neculita et al. (2008) also trialled bioreactor systems, and both studies found similar results to the Bellvue bioreactor, particularly the Behum et al. study, which was using AMD of a similar severity to Bellvue (pH ranging from 2.0-3.0 and higher metal concentrations).

4.5. ALD

This showed a contrasting pattern of metal concentrations compared to the other three treatment systems. There were up to 75% higher metal concentrations in the discharge coming out of the ALD than there were going in, which demonstrates that the ALD was not functioning efficiently and was not treating the AMD to the extent that was required. This is likely due to technical issues and equipment malfunctions that affected it early in the sampling period, which are hypothesized to have caused armouring of the limestone rock filling the ALD.

When flow was re-established through the ALD after these issues were fixed, there was insufficient contact of the AMD with reactive limestone to allow an increase in pH and reduction in dissolved metal concentration, and therefore the AMD travelling through the ALD would not have changed much in terms of the geochemistry. This was observed during the field trials, with the effluent chemistry of the ALD discharge closely shadowing the influent AMD chemistry. Another factor that likely contributed to the increase in metals is the dissolution of precipitates that could have formed on the limestone while the ALD was inactive. Subsequent re-suspension of these in the ALD would lead to higher dissolved metal concentrations between the pool water entering the ALD and the 'treated 'water exiting.

The hydraulic residence time in the ALD was increased to give extended contact with the limestone, but this did not decrease the concentration of dissolved metals within the AMD, or even change the overall water chemistry by much.

The issue of limestone armouring is a well-researched problem that has been documented in multiple ALD treatment studies, because these systems are some of the most vulnerable (Zipper & Skousen 2010). Limestone armouring reduces the reactive surface area of the limestone and decreases its neutralization capacity to around 20% (Skousen et al., 1997). This is consistent with the results from the ALD at Bellvue, which indicate that there was armouring because the dissolved metal concentrations did not decrease after contact with the limestone, as was expected.

4.6. System Issues and Further Work

All four treatment systems installed at Bellvue were affected by operational issues that influenced the quality of the results of the treatment trials.

The biggest problem faced by the three reactor systems was HRT. This was controlled by the influent flow of AMD, which itself was controlled by a series of timer valves that had been programmed to deliver a small amount of AMD to the systems at a specified frequency.

The first HRT issue was caused by the discrepancy between the bioreactor and mussel shell substrate types, which had slightly varying porosities, and therefore different permeabilities. Both systems were fed from the same source of AMD, and the time valve was setup to deliver a specific amount of AMD to each system that was then divided equally between the two. There is a potential issue here because the only way to control how much AMD each system received was via a ball valve on the inflow pipe of each reactor. This valve could be adjusted, but there was no point to measure flow after this point and so there was no way to quantify or guarantee an accurate flow rate into each system.

This created different and varying flow rates within the MSR and the bioreactor, and this influenced the treatment success for each system, especially when the flow rate was too high and HRT was too short, and the AMD did not have the recommended time to react

with the treatment substrate. To avoid this in future, it would be best to give each system an independent supply to make it easier to control the individual flow rate.

The MSO also had issues with flow, although this was because the AMD for this system was sourced from the cascade, where flow rate was very low. To ensure an adequate volume of AMD was available to the system at all times, a small cistern was installed to act a reservoir. This was covered with a mesh that prevented large clumps of moss and soil and leaves from entering, but did not filter the fine-grained material found in the runoff from the cascade. This fine-grained sediment built up in the bottom of the cistern and in the bottom of the ball valve installed on the inflow pipe into the MSO. It had the potential to block the flow into the system, especially over time as the sediment built up. While this blockage was never confirmed, the flow into the reactor was more than halved over the treatment period (which more than doubled the HRT) and resulted in the impressive treatment results from the MSO.

This was a beneficial result, but the inconsistencies in flow between the reducing reactors (MSR and bioreactor) and the MSO created difficulties in making comparisons. Normalizing the HRT made this process easier and gave more useful information about the performance of the mussel shell reactors (comparing how well oxidizing vs. reducing systems worked). Another option going forward would be to improve the AMD delivery system into the MSO, and somehow filter and reduce the amount of sediment entering the system.

The ALD system was operational for most of the sampling period, but it was not performing to the expected standard, and this is likely due to equipment failures and delays at the start of the treatment period. The caps sealing the ALD pipe failed when flow into the system was first started, and in the fortnight that it took to repair them, the ALD sat inactive and full of acidic AMD from the pool. This likely resulted in armouring of the limestone filling the ALD, so that when flow was re-established there was insufficient contact with reactive limestone to allow an increase in pH and reduction in dissolved metal concentration. Re-suspension of precipitates that formed and armoured the limestone in the ALD would lead to higher dissolved metal concentrations in the effluent, as was observed during the trial.

The hydraulic residence time in the ALD was increased to give extended contact with the limestone, but this did not change the overall water chemistry by much, so to improve the

performance of the ALD, it would be useful to open the pipe and drain it completely before replacing the limestone and re-setting the system. Another factor that would have exacerbated this issue was the size of the limestone rock used in the trial. The limestone was roughly sized at 80mm, and this is the size that has been used in previous ALD experiments. However, this system was small-scale, and it would have perhaps been more advisable to use a smaller-sized limestone with a larger reactive surface area to better represent a full-scale example of an ALD. This would have also decreased the degree of armouring that occurred when the ALD was inactive, although not avoided the problem entirely.

4.7. Implications for Remediation

4.7.1. Summary of System Performances

The MSO performed very well for most of the physicochemical parameters measured during the study, but HRT was an important influence in these results. The simple, low-cost materials used to construct this and the MSR system make mussel shell reactors ideal solutions for AMD sites such as Bellvue, with high dissolved metal concentrations and low flow conditions. The MSR, while not performing as well as the MSO in terms of percentage metal removal, was still a viable treatment option at the site. This is because it had half the HRT of the MSO, but reduced metal concentrations by more than 50% in some instances. Again, it was simple to install and apart from adjustments to flow and HRT, required no maintenance.

The Bioreactor was more costly and time-consuming to construct, because it used a variety of materials in the treatment substrate. However, it performed as well as the MSR for some of the chemical parameters measured, and better in others. This system was more affected by inconsistent HRT and flow rates, and this is likely what caused the fluctuations in metal concentrations in the Bioreactor effluent.

The ALD system was operational for most of the sampling period, but it was not performing to the required standard, and this is likely due to equipment failures and delays that inadvertently caused armouring of the limestone in the tube and reduced the reactive

surface area of the limestone in the ALD. This explains the elevated metal concentrations from the AMD exiting the ALD, and the only slightly improved pH from this system.

4.7.2. Bellvue Management

Trumm and Cavanagh (2006) recommended multiple treatment options at Bellvue, based on the existing AMD chemistry, and following the steps laid out in Trumm (2010). The Bellvue Mine site is an abandoned mine, which means that there are no official parties responsible for carrying out AMD remediation at the site, other than the West Coast Regional Council, which has recently published guidelines regarding this (Simcock & Ross, 2014). Because the mine is not currently operating, nor is it expected to in the future, passive treatment is the best option for this site (Trumm 2010). The AMD chemistry at the site allows for both types of passive treatment – oxidising or reducing systems. The pool at site A has a large volume of available water, compared to low volume, variable flow coming down the cascade from the pool. The oxidation process that occurs as this AMD moves down the cascade also oxidizes the metals and ions dissolved in the water. Oxidised metals more readily form precipitates and are more likely to clog treatment system substrate and reduce permeability, thereby reducing the effectiveness of an oxidizing system. For this reason, the pool was chosen as the optimal source of AMD, meaning that reducing passive treatment systems were the best choice to trial at the site.

The type of reducing passive treatment best suited to the site was first alluded to in Trumm & Cavanagh (2006). The initial analyses of AMD undertaken in that study led the authors to suggest using a vertical flow wetland, anaerobic wetland, or ALD to treat the AMD from the pool. However, the results of recent studies (McCauley et al., 2009; Mackenzie et al., 2011; Uster et al., 2013) indicated that using bioreactor and mussel shell treatment systems would be an excellent choice for the Bellvue site, because they were capable of treating AMD with low pH and high metal concentrations. There had been very few field studies undertaken using these systems, and this was an exciting opportunity to investigate their performance at a site like Bellvue. The opportunity also arose to compare an oxidizing mussel shell reactor with a reducing mussel shell reactor.

The results of the small-scale passive treatment systems trialled at Bellvue showed that simple reducing reactors using an alkaline substrate like mussel shell were the most effective and are therefore recommended for treatment. The sulphate-reducing bioreactor treatment system also performed as well as the mussel shell systems, although it was slightly more complex to install and had more problems achieving a consistent HRT, which is a common problem with bioreactors. This influenced the results from that system, which were markedly variable. It is still an alternative that could be used at the site, however.

The ALD was the most difficult to install, because the geometry of the pipe that was used for the system made it awkward to fill and plumb, and the results from the treatment trials were not expected and not up to the standard of the other systems. However, the ALD was affected by mechanical problems which caused its unsatisfactory performance, and as such this system, when functioning properly, could still be an effective and viable treatment option for Bellvue.

4.7.3. Other AMD Sites

All four treatment systems trialled at Bellvue have been used previously to treat AMD at sites either in New Zealand, overseas, or both. ALD's are very common, followed by bioreactors. Mussel shell reactors are relatively new treatment systems, but are a very attractive option for New Zealand conditions because they are effective at treating even severe AMD sites, like Bellvue, and the mussel shell substrate is easy to source in the South Island, and very cost effective.

All four types of systems require enough space for installation, which will limit their suitability at sites with very steep topography and little flat space. However, the reactor systems can be installed in full IBC tanks, compared to the half-sized IBCs used in this study. This makes the reactors suitable for sites with only a small amount of available space.

Further work would need to involve trialling full-scale systems and measuring their performance. The aim of this study was to provide more information about how each of these types of systems would perform when treating AMD with chemistry similar to that found at Bellvue. The systems were not run for very long, so no inferences about the longevity of the systems can be made from the current dataset. It would also be beneficial

to excavate each system and run chemical analyses to determine exactly what precipitates are forming in the substrate and learn exactly how the systems are working to treat the AMD. This will also give clues to the expected life of the system and how long the substrates can be expected to perform for. Unfortunately, timing and financial constraints prevented this work from being undertaken at the Bellvue site.

The small-scale size of each system is a limitation that will need to be accounted for when scaling them up for full treatment size. Trialling the systems with AMD of a different chemistry will also give better understanding of the types of sites they can be used at.

Passive treatment systems are the best option for the Bellvue Mine site, and the results of this study have implications for further work at the site, as well as further afield.

5. Summary and Conclusions

5.1. Project Objectives

Bellvue Mine is an old coal mine located near Rapahoe, West Coast, South Island. This mine has been abandoned for over 40 years and is currently draining acid water with elevated metal concentrations into the nearby waterway, Cannel Creek. The existing knowledge about the background geochemistry of the AMD and Cannel Creek was limited to a single study undertaken in 2006 by which showed that Bellvue was responsible for over 60% of the AMD contamination to Cannel Creek (Trumm & Cavanagh, 2006).

The present research aimed to provide information about the performance of different types of passive AMD treatment systems by trialling a range of small-scale systems at the Bellvue Mine site on the West Coast, South Island. In order to determine the most effective types of treatment systems to use at the site, and how well they performed, it was necessary to have an understanding of the background AMD chemistry at the site and the chemistry of the receiving environment, Cannel Creek. This was undertaken by conducting a geochemical survey at the site and installing trial-scale passive treatment systems based on the results of the survey, then monitoring the performance of these systems.

5.2. Geochemical Issues at the Site

Bellvue Mine is affected by AMD, which can be caused when pyrite in mine workings is exposed to oxygen. This process produced a low pH of 3 and elevated metal concentrations, making the mine drainage uninhabitable for aquatic biota.

To understand how to treat the AMD at the site, the background geochemistry of the site was studied in a 14-month baseline geochemical survey, which comprised water quality testing and water chemistry sampling of both the AMD and Cannel Creek water upstream and downstream of the Bellvue inflow. When the results were analysed, the background AMD chemistry at the site showed several trends:

- pH was very steady at the pool site, maintaining a level just under 2.5, apart from a small fluctuation early in the sampling period.
- Sites downstream of the pool (the top cascade, mid cascade, and bottom cascade) showed increasingly variable pH as other parameters like DO and metal concentrations changed in the discharge.
- The pool site chemistry was more stable than the downstream sites, and this influenced the overall chemical patterns at the site.
- Perturbations to dissolved metal concentrations occurred around the same time at each site, and local precipitation played a part in the chemistry of the AMD.
- The highest metal concentrations at the site were recorded over the summer months, when there was less dilution from precipitation; while the lowest concentrations were recorded in winter/spring, when precipitation was highest.

5.3. Passive Treatment Trials

The chemistry and existing conditions at Bellvue make this site well suited to passive treatment, and when using AMD from the pool site, reducing passive systems are the best options for effective treatment. Based on the recommendations made in Trumm and Cavanagh (2006), and ALD, two mussel shell reactor and one sulphate-reducing bioreactor were installed at the site. The chemistry of the treated discharge from these systems was monitored for a 4-month period.

The results from the various passive treatment systems showed constant variation in both chemistry and hydraulic residence time. In general, the two Mussel Shell reactors and the Bioreactor all reduced the concentration of dissolved metals in the AMD by 60% to 99% compared to the influent AMD chemistry, while dissolved metals from the ALD increased in concentration for the majority of the study. The mussel shell reactor systems were most effective at treating the Bellvue Mine AMD. The sulphate-reducing bioreactor system also performed well, reducing metal concentrations by more than 80% at times, and comparisons between all three systems (at the same HRT) showed very similar results.

Of all the systems that were trialled, the MSO (mussel shell oxidized) was the most effective, which was because the HRT was twice that of the other two reactor systems, and also because of the influent AMD chemistry whereby the metals were oxidized and precipitated more readily.

The mussel shell reduced (MSR) and the bioreactor systems performed well, although the bioreactor was slightly more effective at reducing metal concentrations than the MSR. However, the MSR increased alkalinity and generally improved the quality of the effluent AMD more than the bioreactor.

5.3.1. Conclusions

The study undertaken at Bellvue Mine showed that:

- The Bellvue Mine drainage has a constant low pH (<2.7) that is caused by acid mine drainage
- There are five key metals that have high dissolved concentrations in the mine discharge, particularly Fe which reached 210 mg/L in one sample.
- A mussel shell reactor treating oxidized AMD was the most effective passive treatment method trialled at the site; however there are potential issues with sludge build-up.
- When treating reduced AMD, the bioreactor and mussel shell reactor worked well, but the anoxic limestone drain did not work as well as expected.

5.4. Remediation Issues and Options

All four treatment systems at Bellvue experienced operational problems that affected the results of the treatment study. The MSR and bioreactor were both fed from the same source, but each system had a slightly different permeability, which meant that the flow rate was the same for each but HRT was different. In future, separating the AMD inflow for each will allow greater control and better accuracy of treatment results.

The HRT of the MSO was affected by sediment build-up in the cistern that acted as the AMD source for the reactor. This more than doubled the HRT in the system, which was beneficial

for the treatment results, but created problems when making comparisons between the system performances of all three reactors. Normalizing the HRT allowed for direct comparisons between all three reactors at a 24 hr residence time. This gave more useful information about the performance of the mussel shell reactors (comparing how well oxidizing vs. reducing systems worked). Another option going forward would be to improve the AMD delivery system into the MSO, and reduce the amount of sediment entering the system.

The ALD was affected by operational issues from the start-up period. A failure in one of the caps sealing the ALD when it was being filled for the first time meant that it sat inactive for two weeks, full of acidic mine water. This reacted with the limestone filling the pipe, and the latter was subsequently armoured by iron oxides (?)and other metal precipitates, which will require excavation of the ALD to determine. This effectively prevented the limestone from reacting with any new AMD that was introduced, and so the system overall failed to produce the expected results. To remedy this, the limestone in the ALD would need to be replaced, and perhaps re-sized to a smaller particle size to increase the reactive surface area.

5.5. Future Research

This project has aimed to increase the available information on the performance of these systems in New Zealand conditions, with the hopes that this will be used to help make better informed decisions about the best type of treatment system to use at a site like Bellvue. This research also has wider-ranging implications, because it can be used to expand the existing knowledge about the different types of systems that were used in this study, and their subsequent performance, which will improve the understanding of passive AMD remediation moving forward.

Appendix I

Part (A) of Appendix (I) is attached as an Excel spreadsheet and contains the raw data set from the baseline geochemical surveys of Bellvue Mine AMD and Cannel Creek that were undertaken. All data analysis that was undertaken using these results is included in the spreadsheet.

Part (B) i) Quote Form from Hills Laboratories detailing the various chemical analysis methods used to determine the various parameters for the water chemistry analyses from Bellvue Mine AMD and the passive treatment systems

Part (B) ii) Example of chemical results form received from Hills post-sample analysis. This form is for the background AMD chemistry survey, and includes an example of the quarterly full suite metal analyses that were conducted, and the method standards that were used as guidelines.

Appendix II

Appendix II is attached as an Excel spreadsheet and presents the raw data from the passive treatment trials. This is arranged per system and colour-coded as such. It includes all data analysis that was conducted using the raw data.

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